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CLAIMS

[Claim(s)]

[Claim 1] The metal oxide film which becomes a wafer substrate in a reaction chamber from Ti (titanium) oxide, Zr (zirconium) oxide, or Hf (hafnium) oxide, Or it sets to the cleaning approach of the CVD system which forms the compound metal oxide film containing two or more sorts of these oxides. By contacting the chlorine-based gas which contains a chlorine atom without including a fluorine in said metal oxide film deposited on the interior of said reaction chamber, or said compound metal oxide film The cleaning approach of the CVD system characterized by etching this metal oxide film or this compound metal oxide film, and making the inside of a reaction chamber into clarification.

[Claim 2] The cleaning approach of the CVD system characterized by activating said chlorine-based gas outside said reaction chamber using the plasma or heat energy in the cleaning approach of a CVD system according to claim 1.

[Claim 3] The cleaning approach of the CVD system characterized by activating said chlorine-based gas in said reaction chamber using the plasma or heat energy in the cleaning approach of a CVD system according to claim 1.

[Claim 4] It is the cleaning approach of the CVD system characterized by choosing and using at least one kind of gas of Cl_2 , BCl_3 , and the HCl(s) for said chlorine-based gas in the cleaning approach of a CVD system given in any 1 term among claims 1-3.

[Claim 5] The metal oxide film which becomes Si wafer substrate in a reaction chamber from Ti (titanium) oxide, Zr (zirconium) oxide, or Hf (Hough 2 UMU) oxide, Or it sets to the cleaning approach of the CVD system which forms the compound metal oxide film containing two or more sorts of these oxides. By contacting the chlorine-based gas which contains a chlorine atom in said metal oxide film deposited in said reaction chamber, or said compound metal oxide film as the 1st step The cleaning approach of the CVD system which etches this metal oxide film or this compound metal oxide film, and is characterized by introducing chlorine and the gas which is easy to react in a reaction chamber as the 2nd step.

[Claim 6] The chlorine used at said 2nd step in the cleaning approach of a CVD system according to claim 5 and the gas which is easy to react are the cleaning approach of the CVD system characterized by using either or the both sides of hydrogen gas or a steam.

[Claim 7] The CVD system with which the inside of a reaction chamber is cleaned by any 1 term by the cleaning approach of a publication among claims 1-6.

[Claim 8] The metal oxide film which becomes a wafer substrate in a reaction chamber from Ti (titanium) oxide, Zr (zirconium) oxide, or Hf (hafnium) oxide, Or it sets to the CVD system which forms the compound metal oxide film containing two or more sorts of these oxides. The CVD system characterized by having an activation means to activate the chlorine-based gas contacted to said metal oxide film deposited on the interior of said reaction chamber, or said compound metal oxide film using the plasma or heat energy outside said reaction chamber.

[Claim 9] The metal oxide film which becomes a wafer substrate in a reaction chamber from Ti (titanium) oxide, Zr (zirconium) oxide, or Hf (hafnium) oxide, Or it sets to the CVD system which

forms the compound metal oxide film containing two or more sorts of these oxides. The CVD system characterized by having an activation means to activate the chlorine-based gas contacted to said metal oxide film deposited on the interior of said reaction chamber, or said compound metal oxide film using the plasma or heat energy in said reaction chamber.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a CVD system and its cleaning approach, and relates to the defecation technique of the CVD (Chemical Vapor Deposition) equipment which forms Ti oxide, Zr oxide, Hf oxide, or the metallic oxide chosen from these compound oxide films in substrates, such as Si wafer, especially.

[0002]

[Description of the Prior Art] In order to cut down the power consumption of a semiconductor device, thin film-ization of SiO₂ gate dielectric film is advanced. If SiO₂ gate dielectric film thin-film-izes, the following problems will arise. That is, the leakage current by the direct tunnel effect between a gate electrode and a channel layer increases, and the dependability of dielectric breakdown of gate dielectric film falls further.

[0003] In order to solve this problem, even if it uses the thick film physically as an ingredient which replaces SiO₂, application examination of the high dielectric constant ingredient with which the same electrostatic capacity as SiO₂ is obtained is progressing. Thereby, the leakage current and dielectric breakdown can be suppressed. Specifically as this high dielectric constant gate-dielectric-film ingredient, adoption of a stable oxide is considered by thermodynamics targets, such as Ti oxide, Zr oxide, Hf oxides, or these composites.

[0004] In the CVD system which forms these metallic oxides to substrates, such as a wafer, a metallic oxide accumulates on the internal surface of a reaction chamber etc. like a wafer front face. This deposit becomes easy to separate in the stress which thermal stress and the film itself have from a wall surface, so that alimentation increases. The deposit which separated adheres to a wafer front face by gravity, electrostatic force, a fluid force, etc., and causes an open circuit and short circuit of wiring. Therefore, before such a problem arises, it is necessary to remove a deposit periodically (cleaning).

[0005] As this cleaning approach, as shown in JP,10-199874,A recently, a radical is generated using the source of the plasma established in the location different from a reaction chamber, it is introducing this radical in a reaction chamber, and the so-called remote plasma cleaning which etches and cleans the wall surface deposition film is used abundantly. The description of this approach is that there is no damage by the ion spatter to the wall surface at the time of cleaning etc. in order to gasify and clean a deposit only by the chemical reaction of activated gas.

[0006] Moreover, the approach of cleaning by the gas which contains a halogen or a halogenated compound in JP,10-335318,A for the thin film which contains alkaline earth metal in a configuration element is indicated.

[0007]

[Problem(s) to be Solved by the Invention] However, if it is going to clean Zr oxide, Hf oxide, or this bipolar membrane from the former in remote plasma cleaning of a publication using NF₃ gas currently used abundantly as cleaning gas to above-mentioned JP,10-199874,A, ZrF₄, HfF₄, etc. will be generated as a resultant.

[0008] The vapor pressure of these resultants is dramatically low, for example, in ZrF_4 , vapor pressure is zero mostly in about 0.1Pa and 200 degrees C at 500 degrees C. Since considering that the wall surface temperature at the time of cleaning of a CVD system is 200 degrees C or less a resultant does not evaporate, a deposit can be cleaned. In order to avoid this problem, it is necessary to choose cleaning gas with the high vapor pressure of the resultant generated by the chemical reaction at the time of cleaning.

[0009] Moreover, it has the trouble that a resultant is not evaporated at low temperature and it cannot clean if the vapor pressure of ZrF_4 of a resultant is low when cleaning at low temperature about these metal oxide-films [, such as Ti, Zr, or Hf,] or compound metal oxide film and halogenated compound, for example, NF_3 gas is used for cleaning of Zr oxide, although the cleaning object of an example given in above-mentioned JP,10-335318,A is alkaline earth metal and it completely differs from this invention.

[0010] The object of this invention is to provide the thermodynamics target of Ti oxide deposited on the wall surface in the reaction chamber of a CVD system etc., Zr oxide, Hf oxides, and these composite film with the CVD system which removes a stable high dielectric constant ingredient by etching, and defecates the inside of a reaction chamber, and its cleaning approach.

[0011]

[Means for Solving the Problem] In order to attain the above-mentioned object, the cleaning approach of the CVD system of this invention The metal oxide film which becomes a wafer substrate in a reaction chamber from Ti (titanium) oxide, Zr (zirconium) oxide, or Hf (hafnium) oxide, Or it sets to the cleaning approach of the CVD system which forms the compound metal oxide film containing two or more sorts of these oxides. It is characterized by etching this metal oxide film or this compound metal oxide film, and making the inside of a reaction chamber into clarification by contacting the chlorine-based gas which contains a chlorine atom without including a fluorine in said metal oxide film deposited on the interior of said reaction chamber, or said compound metal oxide film.

[0012] According to this invention persons' knowledge, as a result of investigating the relation between the vapor pressure of the halogenide of Ti, Zr, and Hf, and temperature, compared with ZrF_4 and HfF_4 (fluoride), the vapor pressure of $ZrCl_4$ and $HfCl_4$ (chloride) is far high, vapor pressure is about 100Pa at 200 degrees C, and it turns out that the resultant at the time of cleaning is gasifiable (drawing 1 , 2 reference). Furthermore, it turns out that the vapor pressure of $TiCl_4$ (chloride) has vapor pressure sufficient at 100 degrees C for those with 10000Pa or more, and cleaning (drawing 3).

[0013] Moreover, as for each reaction which generates a chloride at the reaction of a chlorine atom, Ti oxide, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane, it turns out that the difference of the Gibbs free energy before and behind a reaction serves as a negative value, and the reaction of a metallic oxide and chlorine-based cleaning gas tends to progress.

[0014] According to this invention, from the above thing, the resultant generated when not the gas of the fluorine system of NF_3 grade but the gas of a chlorine system is contacted to Ti oxide deposited in the reaction chamber of a CVD system, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane and is etched into them is promptly gasifiable. Therefore, if this gas is exhausted, the inside of a reaction chamber can be defecated easily.

[0015] Moreover, activation of the above-mentioned chlorine-based gas in this invention is possible within and without a reaction chamber, as a CVD system, by installing the activation means of the above-mentioned chlorine-based gas out of a reaction chamber, for example, remote plasma cleaning is attained and the damage at the time of the cleaning in a reaction chamber is controlled. Moreover, if you make it activated in a reaction chamber, simplification and low-cost-izing of equipment will be attained.

[0016]

[Embodiment of the Invention] First, the outline is explained about the cleaning approach of the CVD system of this invention. The object product which carries out etching clearance in this invention is a metallic oxide of Ti oxide, Zr oxide, Hf oxides, and these composites.

[0017] As compared with the vapor pressure of the fluoride of the above-mentioned metal, the cleaning approach of this invention makes chlorine-based gas act on the above-mentioned product for cleaning which the direction of the vapor pressure of a chloride deposits in the reaction chamber of a CVD

system (membrane formation equipment) paying attention to a high point, and is made to carry out etching clearance.

[0018] Hereafter, the cleaning approach of this invention is explained in full detail. Two conditions, that the vapor pressure of the resultant by ** cleaning is high and reacting [a ** metallic oxide and cleaning gas / tend] **, are required for the cleaning gas for carrying out etching clearance of the metallic oxide of Ti oxide deposited on the reaction chamber internal surface of CVD systems, such as semiconductor fabrication machines and equipment, Zr oxide, Hf oxide, and these composites, and defecating the inside of a reaction chamber.

[0019] First, the vapor pressure of the resultant of the above-mentioned ** is examined. Generally, in cleaning, the halogen gas containing reactant high chlorine, a reactant high fluorine, etc. is used. Then, the relation between the vapor pressure of the halogenide of Ti, Zr, and Hf and temperature was investigated. The result is shown in drawing 1 - drawing 3 .

[0020] Compared with ZrF_4 and HfF_4 (fluoride), the vapor pressure of $ZrCl_4$ and $HfCl_4$ (chloride) is far high, vapor pressure is about 100Pa at 200 degrees C, and drawing 1 and drawing 2 show that the resultant at the time of cleaning is gasifiable. Moreover, drawing 3 shows that the vapor pressure of $TiCl_4$ (chloride) has vapor pressure sufficient at 100 degrees C for those with 10000Pa or more, and cleaning.

[0021] The above thing shows that the resultant when etching Ti oxide deposited on the reaction chamber internal surface of a CVD system by using not the gas of the fluorine system of NF_3 grade but the gas of a chlorine system, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane can be gasified and exhausted.

[0022] Next, the ease of progressing of the reaction of the above-mentioned metallic oxide of the above-mentioned ** and cleaning gas is examined. The ease of progressing of a reaction can calculate Gibbs' free energy about each of each metallic oxide, a chlorine atom, and a resultant, and can make an index the value (ΔG) which deducted the Gibbs free energy of the system before a reaction from the Gibbs free energy of the system after a reaction. This ΔG and a reaction equilibrium constant (K) have the relation of a degree type (1), when R is made into a gas constant and they make T the temperature of the system of reaction time.

[0023]

$K \cdot \exp(-\Delta G/RT) \dots (1)$

[0024] From this formula, if ΔG is the value of 0 or +, it can be said that a reaction is in the inclination to hardly progress, but for a reaction to progress, so that ΔG is - and that value is conversely large. At the reaction of a chlorine atom, Ti oxide, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane, as for all, ΔG serves as a negative value, and, as for the reaction which generates a chloride, a reaction progresses.

[0025] From the above thing, by contacting the chlorine-based gas which contains chlorine and chlorine in Ti oxide deposited on an internal surface, piping, etc. of a reaction chamber of a CVD system, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane, etching clearance of these film can be carried out, and the inside of a reaction chamber can be defecated. In addition, it is more desirable not to include a fluorine in cleaning gas, in order to avoid an adverse effect.

[0026] Next, the operation gestalt of the CVD system of this invention is explained using drawing 4 - drawing 6 . The first operation gestalt (refer to drawing 4) activates the chlorine-based gas in this invention in the exterior of a reaction chamber, and introduces it in a reaction chamber. Moreover, the second operation gestalt (refer to drawing 5) activates the chlorine-based gas introduced in the reaction chamber, and should just prepare a power source outside. Moreover, the third operation gestalt (refer to drawing 6) introduces chlorine-based gas into the heated reaction chamber, and activates chlorine-based gas with temperature.

[0027] (The first operation gestalt) Drawing 4 shows the structure and the configuration of a CVD system of the first operation gestalt. A CVD system consists of a reaction chamber 1, a material gas feed zone 31, and the cleaning gas supply section 32. In a reaction chamber 1, desired Ti oxide, Zr oxide, Hf oxide, or the metal oxide film of such bipolar membrane is formed to the wafer substrate 5 (it is also

only called a wafer 5).

[0028] Moreover, in order that the part in contact with cleaning gas, such as the internal surface 2 of a reaction chamber 1, may reduce the damage by cleaning, the ingredient which is tolerant to cleaning gas or surface treatment, for example, alumite processing, hooker nickel passive state processing, etc. are performed.

[0029] In the material gas feed zone 31, the liquid raw material 14 is evaporated and it sends into a reaction chamber 1. As for the liquid raw material 14 extruded by the pressure of helium gas 17, the amount of requests is sent into a carburetor 16 by the liquid massflow controller 15. The sent-in liquid raw material 14 is evaporated within the carburetor 16 held at the elevated temperature.

[0030] This vaporized liquid raw material 14 is introduced in a reaction chamber 1 through piping 41. Piping 41 is heated to desired temperature (about 100-200 degrees C) so that the vaporized liquid raw material 14 may not carry out a reliquefaction. In addition, the amount of requests can also supply O₂ gas 18 in a reaction chamber 1 with a massflow controller 19.

[0031] In the cleaning gas supply section 32, cleaning gas is activated by the plasma and it sends in in a reaction chamber 1. In this invention, the amount of requests is introduced into the source 24 of the remote plasma for Cl₂ gas 20 with massflow controllers 23 and 25 with Ar gas 22.

[0032] It activates with plasma energy and Cl₂ gas 20 introduced into the sources 24 of the remote plasma (RF plasma, mu wave plasma, etc.) is introduced in a reaction chamber 1 through the cleaning gas supply piping 26 by which alumite processing of the inner surface was carried out. Similarly, H₂ gas 21 and Ar gas 22 are also activated, and it can introduce in a reaction chamber 1.

[0033] In this CVD system, the original membrane formation activity which processes two or more wafers, the cleaning in (1) (2) this invention, and the Puri membrane formation activity which is a preparatory work for doing the membrane formation activity of (3) original are repeated successively.

[0034] First, the procedure of the membrane formation activity of the above (1) is explained. A susceptor 3 is lowered and the top-face location is made into the level surface location of the conveyance opening 10. And by opening a gate valve 11, moving a wafer 5 onto a susceptor 3 from the conveyance opening 10, and moving a lifter 8 up with the conveyance arm which is not illustrated, while moving a wafer 5 to reception from a conveyance arm and moving a conveyance arm out of a reaction chamber 1, a gate valve 11 is closed. Next, while lowering a lifter 8, a susceptor 3 is moved up to a membrane formation location.

[0035] At this time, power is supplied to the heater 4 embedded in the susceptor 3 from a feeder 7, and it is raised to the temperature (about 200-700 degrees C) of a request of a wafer 5. Similarly, the reaction chamber wall surface 2 and the shower head 6 are also raised to desired temperature (- 300 degrees C) with a temperature control unit 13.

[0036] Under such temperature setting out, while introducing O₂ gas 18 of the amount of requests in a reaction chamber 1 with the material gas of the amount of requests which evaporated the liquid raw material 14 from the material gas feed zone 31, and a massflow controller 19, it is made the pressure (several 100 - 10000Pa of numbers) of a request of the inside of a reaction chamber 1 with a vacuum pump 12, and need time amount (several minutes) membrane formation is carried out at a wafer 5.

[0037] After suspending the gas supply from the membrane formation gas supply section 31 after forming request thickness, and exhausting the membrane formation gas in a reaction chamber 1, a susceptor 3 is lowered and the top-face location is made into the level surface location of the conveyance opening 10. And a wafer 5 is lifted up with a lifter 8, a gate valve 11 is opened, and a wafer 5 is put on a conveyance arm by moving the conveyance arm which is not illustrated onto a susceptor 3 from the conveyance opening 10, and moving a lifter 8 caudad. And a conveyance arm is moved out of a reaction chamber 1, and a gate valve 11 is closed.

[0038] If multiple times and this wafer membrane formation processing activity are repeated, a metallic oxide will accumulate on the internal surface 2 of a reaction chamber 1 as well as wafer 5 front face. This deposit becomes easy to separate in the stress which thermal stress and the film itself have from a wall surface, so that alimentation increases. The deposit which separated adheres to wafer 5 front face in gravity, electrostatic force, a fluid force, etc., and causes an open circuit and short circuit of wiring.

Therefore, before becoming such a situation, the next cleaning is carried out, in order to remove a deposit and to defecate the inside of a reaction chamber 1.

[0039] The procedure of cleaning of this invention of the above (2) is explained. A susceptor 3 is lowered and the top-face location is made into the level surface location of the conveyance opening 10. And with the lifter 8 to which a gate valve 11 is opened in, it moved onto the susceptor 3 and the covering wafers 40, such as a product made from an alumina, were moved up from the conveyance opening 10 with the conveyance arm which is not illustrated, the covering wafer 40 is moved to reception from a conveyance arm, a conveyance arm is moved out of a reaction chamber 1, and a gate valve 11 is closed. Next, while lowering a lifter 8, a susceptor 3 is moved up to a membrane formation location.

[0040] At this time, a susceptor 3 is made into desired temperature (about 200-700 degrees C) by supplying power to the heater 4 embedded in the susceptor 3 from a feeder 7. Similarly, the reaction chamber wall surface 2 and the shower head 6 are also made into desired temperature (- 300 degrees C) with a temperature control unit 13.

[0041] Under such temperature setting out, while introducing Cl activated from the cleaning gas supply section 32 in the amount reaction chamber 1 of requests, with a vacuum pump 12, the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa), and need time amount (several minutes) cleaning is carried out. Cl remains on the reaction chamber wall surface 2 after cleaning, and ***** possibility is in the next membrane formation about an adverse effect.

[0042] Therefore, after suspending supply of gas after cleaning termination and exhausting the cleaning gas in a reaction chamber 1, While introducing the amount of requests into the source 24 of the remote plasma for 32Hcleaning gas supply section 2 (hydrogen) gas 21 with a massflow controller 25, activating H2 gas 21 with plasma energy and introducing into a reaction chamber 1 With a vacuum pump 12, the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa), and need time amount (several minutes) cleaning is carried out. Cl which remains on reaction chamber 1 wall surface now reacts with H, and is exhausted outside a reaction chamber 1 as HCl gas.

[0043] Then, a susceptor 3 is made lowering, the top-face location is made into the level surface location of the conveyance opening 10, and the covering wafer 40 is lifted up with a lifter 8, next a gate valve 11 is opened, and the covering wafer 40 is put on a conveyance arm by moving the conveyance arm which is not illustrated onto a susceptor 3 from the conveyance opening 10, and moving a lifter 8 caudad. And while moving a conveyance arm out of a reaction chamber 1, a gate valve 11 is closed. Now, cleaning is completed.

[0044] Thus, since it is efficiently removable at the temperature of a request of Ti oxide deposited on the internal surface 2 of a reaction chamber 1, Zr oxide, Hf oxide, or the deposition film of such bipolar membrane according to this operation gestalt, an equipment stop time can be shortened and it is effective in an equipment operating ratio being referred to as being able to improve.

[0045] In addition, although membrane formation conditions, such as membrane formation time amount, temperature, and a pressure, differ, since the procedures of the Puri membrane formation activity of the above (3) are the almost same work habits as the membrane formation activity of the above (1), they omit explanation here. The object of this activity is for securing the stability of future membrane formation by making containment and a front face smooth for the residual gas of the reaction chamber internal surface 2 after cleaning.

[0046] (The second operation gestalt) Drawing 5 shows the structure and the configuration of a CVD system of the second operation gestalt. The main components of a CVD system are a reaction chamber 1, the material gas feed zone 31, the cleaning gas supply section 33, and RF plasma section 34.

[0047] The reaction chamber 1 has insulated the reaction chamber upper part electrically with the electric insulating plate 29 so that RF plasma can be generated in a reaction chamber 1 at the time of cleaning. The RF power source 28 and matching box 27 which constitute RF plasma section 34 in this reaction chamber upper part are connected.

[0048] In the material gas feed zone 31, the liquid raw material 14 is evaporated and it sends into a reaction chamber 1. As for the liquid raw material 14 extruded by the pressure of helium gas 17, the

amount of requests is sent into a carburetor 16 by the liquid massflow controller 15. The sent-in liquid raw material 14 is evaporated within the carburetor 16 held at the elevated temperature.

[0049] This vaporized liquid raw material 14 is introduced in a reaction chamber 1 through piping 41. Piping 41 is heated to desired temperature (about 100-200 degrees C) so that the vaporized liquid raw material 14 may not liquefy. In addition, O₂ gas 18 can also be supplied in the amount reaction chamber 1 of requests with a massflow controller 19.

[0050] In the cleaning gas supply section 33, Cl₂ gas 20 in this invention and H₂ gas 21 are adjusted in the amount of requests with a massflow controller 25, and are introduced in a reaction chamber 1 through a charging line.

[0051] With the CVD system of this second operation gestalt as well as the first operation gestalt, (1) membrane formation activity (two or more sheet wafer processing), (2) cleaning activities, and (3) Puri membrane formation activity are repeated successively.

[0052] The procedure of the membrane formation activity of the above (1) is the same as that of the above-mentioned first operation gestalt. One by one, if this membrane formation processing activity is repeated, a metallic oxide will accumulate on the internal surface of a reaction chamber 1 as well as wafer 5 front face. This deposit becomes easy to separate in the stress which thermal stress and the film itself have from a wall surface, so that alimentation increases.

[0053] The deposit which separated adheres to a wafer front face by gravity, electrostatic force, a fluid force, etc., and causes an open circuit and short circuit of wiring. Therefore, before becoming such a situation, cleaning for removing a deposit and defecating the inside of a reaction chamber 1 is carried out.

[0054] The procedure of cleaning of the above (2) is explained. First, a susceptor 3 is moved and the covering wafer 40 is moved to reception and a membrane formation location. At this time, it is made the temperature (about 200-700 degrees C) of a request of a susceptor 3 at the heater 4 embedded in the susceptor 3, and reaction chamber 1 wall surface and the shower head 6 are similarly made into desired temperature (- 300 degrees C) with a temperature control unit 13. Since the above is the same as that of the first operation gestalt, detailed explanation is omitted.

[0055] Under such temperature setting out, with this operation gestalt, in order to activate chlorine-based cleaning gas in a reaction chamber, while introducing the amount of requests of Cl₂ gas 20 in a reaction chamber 1 from the cleaning gas supply section 33, it is made the pressure (several 10000Pa) of a request of the inside of a reaction chamber 1 with a vacuum pump 12.

[0056] Subsequently, power (several 100-several kW) is supplied from the RF power source 28. Thereby, Cl plasma is generated in a reaction chamber 1, etching clearance of the deposit is carried out by that activated Cl reacts with the deposit of reaction chamber 1 wall surface, and spatter operation, and the inside of a reaction chamber 1 is cleaned. Cl remains on reaction chamber 1 wall surface after cleaning, and ***** possibility is in the next membrane formation about an adverse effect.

[0057] Therefore, after suspending supply of gas after cleaning termination and exhausting the cleaning gas in a reaction chamber 1, while a massflow controller 25 adjusts 33Hcleaning gas supply section 2 gas 21 in the amount of requests and introducing into a reaction chamber 1, with a vacuum pump 12, the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa), and is cleaned. Now, Cl which remains on reaction chamber 1 wall surface by cleaning reacts with H, and is exhausted outside a reaction chamber as HCl gas.

[0058] Then, like the first operation gestalt, a susceptor 3 is moved, the covering wafer 40 is taken out outside a reaction chamber 1 by the conveyance arm, a gate valve 11 is closed, and cleaning is ended.

[0059] Thus, since Ti oxide deposited on the internal surface 2 of a reaction chamber 1, Zr oxide, Hf oxide, or the deposition film of such bipolar membrane is efficiently removable at desired temperature according to this operation gestalt, an equipment stop time can be shortened and it is effective in the ability to improve an equipment operating ratio.

[0060] Although the procedure of the Puri membrane formation activity of the above (3) is the same as that of the membrane formation activity of the above (1) almost, membrane formation conditions, such as membrane formation time amount, temperature, and a pressure, differ. The object of this activity is

for securing the stability of future membrane formation by making containment and a front face smooth for the residual gas of the reaction chamber internal surface 2 after cleaning.

[0061] (The third operation gestalt) Drawing 6 shows the structure and the configuration of a CVD system of the third operation gestalt. The main components of a CVD system are a reaction chamber 1, the material gas feed zone 31, and the cleaning gas supply section 33. In a reaction chamber 1, desired Ti oxide, Zr oxide, Hf oxide, or the metal oxide film of such bipolar membrane is formed to a wafer 5.

[0062] Supply of material gas is the same as that of the first operation gestalt. That is, in the material gas feed zone 31, after the amount of requests evaporates the liquid raw material 14 extruded by the pressure of helium gas 17 with a carburetor 16, it is introduced in a reaction chamber 1. Piping 41 is heated to desired temperature (about 100-200 degrees C) so that material gas may not liquefy. In addition, the amount of requests can also supply O₂ gas 18 in a reaction chamber 1 with a massflow controller 19.

[0063] In the cleaning gas supply section 33 in this operation gestalt, a massflow controller 25 adjusts ClF gas 35 in the amount of requests, and it introduces in a reaction chamber 1 through a charging line.

[0064] (One) membrane formation activity (two or more sheet wafer processing), (2) cleaning activities, and (3) Puri membrane formation activity are successively repeated like [the CVD system of this third operation gestalt] the above-mentioned first and second operation gestalten.

[0065] About the procedure of the membrane formation activity of the above (1), since it is the same as that of the above-mentioned first operation gestalt, explanation is omitted. One by one, if this membrane formation processing activity is repeated, a metallic oxide will accumulate on the internal surface of a reaction chamber 1 as well as wafer 5 front face. This deposit becomes easy to separate in the stress which thermal stress and the film itself have from a wall surface, so that alimentation increases. The deposit which separated adheres to a wafer front face in gravity, electrostatic force, and a fluid force, and causes an open circuit and short circuit of wiring. Therefore, before becoming such a situation, cleaning for removing a deposit and defecating the inside of a reaction chamber 1 is carried out.

[0066] The procedure of cleaning of the above (2) is explained. Since installation of the covering wafer 40, setting out of the request temperature (about 200-700 degrees C) of a susceptor 3 and the request temperature (- 300 degrees C) of reaction chamber 1 wall surface and the shower head 6, etc. are the same as that of the above-mentioned first and second operation gestalten, explanation is omitted.

[0067] With this operation gestalt, under such temperature setting out, if the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa) with a vacuum pump 12 while introducing ClF gas 35 in the amount reaction chamber 1 of requests from the cleaning gas supply section 33, when ClF gas 35 is activated with heat energy, etching clearance of the deposit will be carried out and the inside of a reaction chamber 1 will be cleaned.

[0068] Since Cl remains on reaction chamber 1 wall surface after cleaning and ***** possibility is in the next membrane formation about an adverse effect, Like the operation gestalt of the above second, while introducing the hydrogen gas 21 of the cleaning gas supply section into a reaction chamber 1 after exhausting the cleaning gas in a reaction chamber 1 If the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa), Residual Cl will react with H and will be exhausted outside a reaction chamber as HCl gas.

[0069] Then, like the above-mentioned first and second operation gestalten, a susceptor 3 is moved, the covering wafer 40 is taken out from the conveyance opening 10, and a gate valve 11 is closed. Now, cleaning is completed.

[0070] Thus, since Ti oxide deposited on the internal surface 2 of a reaction chamber 1, Zr oxide, Hf oxide, or the deposition film of such bipolar membrane is efficiently removable according to this operation gestalt, an equipment stop time can be shortened and it is effective in an equipment operating ratio being referred to as being able to improve.

[0071] Next, although the procedure of the Puri membrane formation activity of the above (3) is the same as that of the membrane formation activity of the above (1) almost, membrane formation conditions, such as membrane formation time amount, temperature, and a pressure, differ. When the object of this activity makes containment and a front face smooth for the residual gas of the reaction chamber internal surface 2 after cleaning, it is as above-mentioned that it is for securing the stability of

future membrane formation.

[0072]

[Effect of the Invention] Since a stable high dielectric constant ingredient is efficiently removable by etching on the thermodynamics target of Ti oxide deposited on the wall surface in the reaction chamber of a CVD system etc., Zr oxide, Hf oxides, and these composite film according to this invention as stated above, an equipment stop time can be shortened and it is effective in an equipment operating ratio being referred to as being able to improve.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to a CVD system and its cleaning approach, and relates to the defecation technique of the CVD (Chemical Vapor Deposition) equipment which forms Ti oxide, Zr oxide, Hf oxide, or the metallic oxide chosen from these compound oxide films in substrates, such as Si wafer, especially.

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PRIOR ART

[Description of the Prior Art] In order to cut down the power consumption of a semiconductor device, thin film-ization of SiO₂ gate dielectric film is advanced. If SiO₂ gate dielectric film thin-film-izes, the following problems will arise. That is, the leakage current by the direct tunnel effect between a gate electrode and a channel layer increases, and the dependability of dielectric breakdown of gate dielectric film falls further.

[0003] In order to solve this problem, even if it uses the thick film physically as an ingredient which replaces SiO₂, application examination of the high dielectric constant ingredient with which the same electrostatic capacity as SiO₂ is obtained is progressing. Thereby, the leakage current and dielectric breakdown can be suppressed. Specifically as this high dielectric constant gate-dielectric-film ingredient, adoption of a stable oxide is considered by thermodynamics targets, such as Ti oxide, Zr oxide, Hf oxides, or these composites.

[0004] In the CVD system which forms these metallic oxides to substrates, such as a wafer, a metallic oxide accumulates on the internal surface of a reaction chamber etc. like a wafer front face. This deposit becomes easy to separate in the stress which thermal stress and the film itself have from a wall surface, so that alimentation increases. The deposit which separated adheres to a wafer front face by gravity, electrostatic force, a fluid force, etc., and causes an open circuit and short circuit of wiring. Therefore, before such a problem arises, it is necessary to remove a deposit periodically (cleaning).

[0005] As this cleaning approach, as shown in JP,10-199874,A recently, a radical is generated using the source of the plasma established in the location different from a reaction chamber, it is introducing this radical in a reaction chamber, and the so-called remote plasma cleaning which etches and cleans the wall surface deposition film is used abundantly. The description of this approach is that there is no damage by the ion spatter to the wall surface at the time of cleaning etc. in order to gasify and clean a deposit only by the chemical reaction of activated gas.

[0006] Moreover, the approach of cleaning by the gas which contains a halogen or a halogenated compound in JP,10-335318,A for the thin film which contains alkaline earth metal in a configuration element is indicated.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since a stable high dielectric constant ingredient is efficiently removable by etching on the thermodynamics target of Ti oxide deposited on the wall surface in the reaction chamber of a CVD system etc., Zr oxide, Hf oxides, and these composite film according to this invention as stated above, an equipment stop time can be shortened and it is effective in an equipment operating ratio being referred to as being able to improve.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, if it is going to clean Zr oxide, Hf oxide, or this bipolar membrane from the former in remote plasma cleaning of a publication using NF₃ gas currently used abundantly as cleaning gas to above-mentioned JP,10-199874,A, ZrF₄, HfF₄, etc. will be generated as a resultant.

[0008] The vapor pressure of these resultants is dramatically low, for example, in ZrF₄, vapor pressure is zero mostly in about 0.1Pa and 200 degrees C at 500 degrees C. Since considering that the wall surface temperature at the time of cleaning of a CVD system is 200 degrees C or less a resultant does not evaporate, a deposit can be cleaned. In order to avoid this problem, it is necessary to choose cleaning gas with the high vapor pressure of the resultant generated by the chemical reaction at the time of cleaning.

[0009] Moreover, it has the trouble that a resultant is not evaporated at low temperature and it cannot clean if the vapor pressure of ZrF₄ of a resultant is low when cleaning at low temperature about these metal oxide-films [, such as Ti, Zr, or Hf,] or compound metal oxide film and halogenated compound, for example, NF₃ gas is used for cleaning of Zr oxide, although the cleaning object of an example given in above-mentioned JP,10-335318,A is alkaline earth metal and it completely differs from this invention.

[0010] The object of this invention is to provide the thermodynamics target of Ti oxide deposited on the wall surface in the reaction chamber of a CVD system etc., Zr oxide, Hf oxides, and these composite film with the CVD system which removes a stable high dielectric constant ingredient by etching, and defecates the inside of a reaction chamber, and its cleaning approach.

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MEANS

[Means for Solving the Problem] In order to attain the above-mentioned object, the cleaning approach of the CVD system of this invention The metal oxide film which becomes a wafer substrate in a reaction chamber from Ti (titanium) oxide, Zr (zirconium) oxide, or Hf (hafnium) oxide, Or it sets to the cleaning approach of the CVD system which forms the compound metal oxide film containing two or more sorts of these oxides. It is characterized by etching this metal oxide film or this compound metal oxide film, and making the inside of a reaction chamber into clarification by contacting the chlorine-based gas which contains a chlorine atom without including a fluorine in said metal oxide film deposited on the interior of said reaction chamber, or said compound metal oxide film.

[0012] According to this invention persons' knowledge, as a result of investigating the relation between the vapor pressure of the halogenide of Ti, Zr, and Hf, and temperature, compared with ZrF₄ and HfF₄ (fluoride), the vapor pressure of ZrCl₄ and HfCl₄ (chloride) is far high, vapor pressure is about 100Pa at 200 degrees C, and it turns out that the resultant at the time of cleaning is gasifiable (drawing 1 ; 2 reference). Furthermore, it turns out that the vapor pressure of TiCl₄ (chloride) has vapor pressure sufficient at 100 degrees C for those with 10000Pa or more, and cleaning (drawing 3).

[0013] Moreover, as for each reaction which generates a chloride at the reaction of a chlorine atom, Ti oxide, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane, it turns out that the difference of the Gibbs free energy before and behind a reaction serves as a negative value, and the reaction of a metallic oxide and chlorine-based cleaning gas tends to progress.

[0014] According to this invention, from the above thing, the resultant generated when not the gas of the fluorine system of NF₃ grade but the gas of a chlorine system is contacted to Ti oxide deposited in the reaction chamber of a CVD system, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane and is etched into them is promptly gasifiable. Therefore, if this gas is exhausted, the inside of a reaction chamber can be defecated easily.

[0015] Moreover, activation of the above-mentioned chlorine-based gas in this invention is possible within and without a reaction chamber, as a CVD system, by installing the activation means of the above-mentioned chlorine-based gas out of a reaction chamber, for example, remote plasma cleaning is attained and the damage at the time of the cleaning in a reaction chamber is controlled. Moreover, if you make it activated in a reaction chamber, simplification and low-cost-izing of equipment will be attained.

[0016]

[Embodiment of the Invention] First, the outline is explained about the cleaning approach of the CVD system of this invention. The object product which carries out etching clearance in this invention is a metallic oxide of Ti oxide, Zr oxide, Hf oxides, and these composites.

[0017] As compared with the vapor pressure of the fluoride of the above-mentioned metal, the cleaning approach of this invention makes chlorine-based gas act on the above-mentioned product for cleaning which the direction of the vapor pressure of a chloride deposits in the reaction chamber of a CVD system (membrane formation equipment) paying attention to a high point, and is made to carry out etching clearance.

[0018] Hereafter, the cleaning approach of this invention is explained in full detail. Two conditions, that

the vapor pressure of the resultant by ** cleaning is high and reacting [a ** metallic oxide and cleaning gas / tend] **, are required for the cleaning gas for carrying out etching clearance of the metallic oxide of Ti oxide deposited on the reaction chamber internal surface of CVD systems, such as semiconductor fabrication machines and equipment, Zr oxide, Hf oxide, and these composites, and defecating the inside of a reaction chamber.

[0019] First, the vapor pressure of the resultant of the above-mentioned ** is examined. Generally, in cleaning, the halogen gas containing reactant high chlorine, a reactant high fluorine, etc. is used. Then, the relation between the vapor pressure of the halogenide of Ti, Zr, and Hf and temperature was investigated. The result is shown in drawing 1 - drawing 3 .

[0020] Compared with ZrF_4 and HfF_4 (fluoride), the vapor pressure of $ZrCl_4$ and $HfCl_4$ (chloride) is far high, vapor pressure is about 100Pa at 200 degrees C, and drawing 1 and drawing 2 show that the resultant at the time of cleaning is gasifiable. Moreover, drawing 3 shows that the vapor pressure of $TiCl_4$ (chloride) has vapor pressure sufficient at 100 degrees C for those with 10000Pa or more, and cleaning.

[0021] The above thing shows that the resultant when etching Ti oxide deposited on the reaction chamber internal surface of a CVD system by using not the gas of the fluorine system of NF_3 grade but the gas of a chlorine system, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane can be gasified and exhausted.

[0022] Next, the ease of progressing of the reaction of the above-mentioned metallic oxide of the above-mentioned ** and cleaning gas is examined. The ease of progressing of a reaction can calculate Gibbs' free energy about each of each metallic oxide, a chlorine atom, and a resultant, and can make an index the value (ΔG) which deducted the Gibbs free energy of the system before a reaction from the Gibbs free energy of the system after a reaction. This ΔG and a reaction equilibrium constant (K) have the relation of a degree type (1), when R is made into a gas constant and they make T the temperature of the system of reaction time.

[0023]

$K \cdot \exp(-\Delta G/RT) \dots (1)$

[0024] From this formula, if ΔG is the value of 0 or +, it can be said that a reaction is in the inclination to hardly progress, but for a reaction to progress, so that ΔG is - and that value is conversely large. At the reaction of a chlorine atom, Ti oxide, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane, as for all, ΔG serves as a negative value, and, as for the reaction which generates a chloride, a reaction progresses.

[0025] From the above thing, by contacting the chlorine-based gas which contains chlorine and chlorine in Ti oxide deposited on an internal surface, piping, etc. of a reaction chamber of a CVD system, Zr oxide, Hf oxide, and the metallic oxide of such bipolar membrane, etching clearance of these film can be carried out, and the inside of a reaction chamber can be defecated. In addition, it is more desirable not to include a fluorine in cleaning gas, in order to avoid an adverse effect.

[0026] Next, the operation gestalt of the CVD system of this invention is explained using drawing 4 - drawing 6 . The first operation gestalt (refer to drawing 4) activates the chlorine-based gas in this invention in the exterior of a reaction chamber, and introduces it in a reaction chamber. Moreover, the second operation gestalt (refer to drawing 5) activates the chlorine-based gas introduced in the reaction chamber, and should just prepare a power source outside. Moreover, the third operation gestalt (refer to drawing 6) introduces chlorine-based gas into the heated reaction chamber, and activates chlorine-based gas with temperature.

[0027] (The first operation gestalt) Drawing 4 shows the structure and the configuration of a CVD system of the first operation gestalt. A CVD system consists of a reaction chamber 1, a material gas feed zone 31, and the cleaning gas supply section 32. In a reaction chamber 1, desired Ti oxide, Zr oxide, Hf oxide, or the metal oxide film of such bipolar membrane is formed to the wafer substrate 5 (it is also only called a wafer 5).

[0028] Moreover, in order that the part in contact with cleaning gas, such as the internal surface 2 of a reaction chamber 1, may reduce the damage by cleaning, the ingredient which is tolerant to cleaning gas

or surface treatment, for example, alumite processing, hooker nickel passive state processing, etc. are performed.

[0029] In the material gas feed zone 31, the liquid raw material 14 is evaporated and it sends into a reaction chamber 1. As for the liquid raw material 14 extruded by the pressure of helium gas 17, the amount of requests is sent into a carburetor 16 by the liquid massflow controller 15. The sent-in liquid raw material 14 is evaporated within the carburetor 16 held at the elevated temperature.

[0030] This vaporized liquid raw material 14 is introduced in a reaction chamber 1 through piping 41. Piping 41 is heated to desired temperature (about 100-200 degrees C) so that the vaporized liquid raw material 14 may not carry out a reliquefaction. In addition, the amount of requests can also supply O₂ gas 18 in a reaction chamber 1 with a massflow controller 19.

[0031] In the cleaning gas supply section 32, cleaning gas is activated by the plasma and it sends in in a reaction chamber 1. In this invention, the amount of requests is introduced into the source 24 of the remote plasma for Cl₂ gas 20 with massflow controllers 23 and 25 with Ar gas 22.

[0032] It activates with plasma energy and Cl₂ gas 20 introduced into the sources 24 of the remote plasma (RF plasma, mu wave plasma, etc.) is introduced in a reaction chamber 1 through the cleaning gas supply piping 26 by which alumite processing of the inner surface was carried out. Similarly, H₂ gas 21 and Ar gas 22 are also activated, and it can introduce in a reaction chamber 1.

[0033] In this CVD system, the original membrane formation activity which processes two or more wafers, the cleaning in (1) (2) this invention, and the Puri membrane formation activity which is a preparatory work for doing the membrane formation activity of (3) original are repeated successively.

[0034] First, the procedure of the membrane formation activity of the above (1) is explained. A susceptor 3 is lowered and the top-face location is made into the level surface location of the conveyance opening 10. And by opening a gate valve 11, moving a wafer 5 onto a susceptor 3 from the conveyance opening 10, and moving a lifter 8 up with the conveyance arm which is not illustrated, while moving a wafer 5 to reception from a conveyance arm and moving a conveyance arm out of a reaction chamber 1, a gate valve 11 is closed. Next, while lowering a lifter 8, a susceptor 3 is moved up to a membrane formation location.

[0035] At this time, power is supplied to the heater 4 embedded in the susceptor 3 from a feeder 7, and it is raised to the temperature (about 200-700 degrees C) of a request of a wafer 5. Similarly, the reaction chamber wall surface 2 and the shower head 6 are also raised to desired temperature (- 300 degrees C) with a temperature control unit 13.

[0036] Under such temperature setting out, while introducing O₂ gas 18 of the amount of requests in a reaction chamber 1 with the material gas of the amount of requests which evaporated the liquid raw material 14 from the material gas feed zone 31, and a massflow controller 19, it is made the pressure (several 100 - 10000Pa of numbers) of a request of the inside of a reaction chamber 1 with a vacuum pump 12, and need time amount (several minutes) membrane formation is carried out at a wafer 5.

[0037] After suspending the gas supply from the membrane formation gas supply section 31 after forming request thickness, and exhausting the membrane formation gas in a reaction chamber 1, a susceptor 3 is lowered and the top-face location is made into the level surface location of the conveyance opening 10. And a wafer 5 is lifted up with a lifter 8, a gate valve 11 is opened, and a wafer 5 is put on a conveyance arm by moving the conveyance arm which is not illustrated onto a susceptor 3 from the conveyance opening 10, and moving a lifter 8 caudad. And a conveyance arm is moved out of a reaction chamber 1, and a gate valve 11 is closed.

[0038] If multiple times and this wafer membrane formation processing activity are repeated, a metallic oxide will accumulate on the internal surface 2 of a reaction chamber 1 as well as wafer 5 front face. This deposit becomes easy to separate in the stress which thermal stress and the film itself have from a wall surface, so that alimentation increases. The deposit which separated adheres to wafer 5 front face in gravity, electrostatic force, a fluid force, etc., and causes an open circuit and short circuit of wiring. Therefore, before becoming such a situation, the next cleaning is carried out, in order to remove a deposit and to defecate the inside of a reaction chamber 1.

[0039] The procedure of cleaning of this invention of the above (2) is explained. A susceptor 3 is

lowered and the top-face location is made into the level surface location of the conveyance opening 10. And with the lifter 8 to which a gate valve 11 is opened in, it moved onto the susceptor 3 and the covering wafers 40, such as a product made from an alumina, were moved up from the conveyance opening 10 with the conveyance arm which is not illustrated, the covering wafer 40 is moved to reception from a conveyance arm, a conveyance arm is moved out of a reaction chamber 1, and a gate valve 11 is closed. Next, while lowering a lifter 8, a susceptor 3 is moved up to a membrane formation location.

[0040] At this time, a susceptor 3 is made into desired temperature (about 200-700 degrees C) by supplying power to the heater 4 embedded in the susceptor 3 from a feeder 7. Similarly, the reaction chamber wall surface 2 and the shower head 6 are also made into desired temperature (- 300 degrees C) with a temperature control unit 13.

[0041] Under such temperature setting out, while introducing Cl activated from the cleaning gas supply section 32 in the amount reaction chamber 1 of requests, with a vacuum pump 12, the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa), and need time amount (several minutes) cleaning is carried out. Cl remains on the reaction chamber wall surface 2 after cleaning, and ***** possibility is in the next membrane formation about an adverse effect.

[0042] Therefore, after suspending supply of gas after cleaning termination and exhausting the cleaning gas in a reaction chamber 1, While introducing the amount of requests into the source 24 of the remote plasma for 32Hcleaning gas supply section 2 (hydrogen) gas 21 with a massflow controller 25, activating H2 gas 21 with plasma energy and introducing into a reaction chamber 1 With a vacuum pump 12, the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa), and need time amount (several minutes) cleaning is carried out. Cl which remains on reaction chamber 1 wall surface now reacts with H, and is exhausted outside a reaction chamber 1 as HCl gas.

[0043] Then, a susceptor 3 is made lowering, the top-face location is made into the level surface location of the conveyance opening 10, and the covering wafer 40 is lifted up with a lifter 8, next a gate valve 11 is opened, and the covering wafer 40 is put on a conveyance arm by moving the conveyance arm which is not illustrated onto a susceptor 3 from the conveyance opening 10, and moving a lifter 8 caudad. And while moving a conveyance arm out of a reaction chamber 1, a gate valve 11 is closed. Now, cleaning is completed.

[0044] Thus, since it is efficiently removable at the temperature of a request of Ti oxide deposited on the internal surface 2 of a reaction chamber 1, Zr oxide, Hf oxide, or the deposition film of such bipolar membrane according to this operation gestalt, an equipment stop time can be shortened and it is effective in an equipment operating ratio being referred to as being able to improve.

[0045] In addition, although membrane formation conditions, such as membrane formation time amount, temperature, and a pressure, differ, since the procedures of the Puri membrane formation activity of the above (3) are the almost same work habits as the membrane formation activity of the above (1), they omit explanation here. The object of this activity is for securing the stability of future membrane formation by making containment and a front face smooth for the residual gas of the reaction chamber internal surface 2 after cleaning.

[0046] (The second operation gestalt) Drawing 5 shows the structure and the configuration of a CVD system of the second operation gestalt. The main components of a CVD system are a reaction chamber 1, the material gas feed zone 31, the cleaning gas supply section 33, and RF plasma section 34.

[0047] The reaction chamber 1 has insulated the reaction chamber upper part electrically with the electric insulating plate 29 so that RF plasma can be generated in a reaction chamber 1 at the time of cleaning. The RF power source 28 and matching box 27 which constitute RF plasma section 34 in this reaction chamber upper part are connected.

[0048] In the material gas feed zone 31, the liquid raw material 14 is evaporated and it sends into a reaction chamber 1. As for the liquid raw material 14 extruded by the pressure of helium gas 17, the amount of requests is sent into a carburetor 16 by the liquid massflow controller 15. The sent-in liquid raw material 14 is evaporated within the carburetor 16 held at the elevated temperature.

[0049] This vaporized liquid raw material 14 is introduced in a reaction chamber 1 through piping 41.

Piping 41 is heated to desired temperature (about 100-200 degrees C) so that the vaporized liquid raw material 14 may not liquefy. In addition, O₂ gas 18 can also be supplied in the amount reaction chamber 1 of requests with a massflow controller 19.

[0050] In the cleaning gas supply section 33, Cl₂ gas 20 in this invention and H₂ gas 21 are adjusted in the amount of requests with a massflow controller 25, and are introduced in a reaction chamber 1 through a charging line.

[0051] With the CVD system of this second operation gestalt as well as the first operation gestalt, (1) membrane formation activity (two or more sheet wafer processing), (2) cleaning activities, and (3) Puri membrane formation activity are repeated successively.

[0052] The procedure of the membrane formation activity of the above (1) is the same as that of the above-mentioned first operation gestalt. One by one, if this membrane formation processing activity is repeated, a metallic oxide will accumulate on the internal surface of a reaction chamber 1 as well as wafer 5 front face. This deposit becomes easy to separate in the stress which thermal stress and the film itself have from a wall surface, so that alimentation increases.

[0053] The deposit which separated adheres to a wafer front face by gravity, electrostatic force, a fluid force, etc., and causes an open circuit and short circuit of wiring. Therefore, before becoming such a situation, cleaning for removing a deposit and defecating the inside of a reaction chamber 1 is carried out.

[0054] The procedure of cleaning of the above (2) is explained. First, a susceptor 3 is moved and the covering wafer 40 is moved to reception and a membrane formation location. At this time, it is made the temperature (about 200-700 degrees C) of a request of a susceptor 3 at the heater 4 embedded in the susceptor 3, and reaction chamber 1 wall surface and the shower head 6 are similarly made into desired temperature (- 300 degrees C) with a temperature control unit 13. Since the above is the same as that of the first operation gestalt, detailed explanation is omitted.

[0055] Under such temperature setting out, with this operation gestalt, in order to activate chlorine-based cleaning gas in a reaction chamber, while introducing the amount of requests of Cl₂ gas 20 in a reaction chamber 1 from the cleaning gas supply section 33, it is made the pressure (several 10000Pa) of a request of the inside of a reaction chamber 1 with a vacuum pump 12.

[0056] Subsequently, power (several 100-several kW) is supplied from the RF power source 28. Thereby, Cl plasma is generated in a reaction chamber 1, etching clearance of the deposit is carried out by that activated Cl reacts with the deposit of reaction chamber 1 wall surface, and spatter operation, and the inside of a reaction chamber 1 is cleaned. Cl remains on reaction chamber 1 wall surface after cleaning, and ***** possibility is in the next membrane formation about an adverse effect.

[0057] Therefore, after suspending supply of gas after cleaning termination and exhausting the cleaning gas in a reaction chamber 1, while a massflow controller 25 adjusts 33Hcleaning gas supply section 2 gas 21 in the amount of requests and introducing into a reaction chamber 1, with a vacuum pump 12, the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa), and is cleaned. Now, Cl which remains on reaction chamber 1 wall surface by cleaning reacts with H, and is exhausted outside a reaction chamber as HCl gas.

[0058] Then, like the first operation gestalt, a susceptor 3 is moved, the covering wafer 40 is taken out outside a reaction chamber 1 by the conveyance arm, a gate valve 11 is closed, and cleaning is ended.

[0059] Thus, since Ti oxide deposited on the internal surface 2 of a reaction chamber 1, Zr oxide, Hf oxide, or the deposition film of such bipolar membrane is efficiently removable at desired temperature according to this operation gestalt, an equipment stop time can be shortened and it is effective in the ability to improve an equipment operating ratio.

[0060] Although the procedure of the Puri membrane formation activity of the above (3) is the same as that of the membrane formation activity of the above (1) almost, membrane formation conditions, such as membrane formation time amount, temperature, and a pressure, differ. The object of this activity is for securing the stability of future membrane formation by making containment and a front face smooth for the residual gas of the reaction chamber internal surface 2 after cleaning.

[0061] (The third operation gestalt) Drawing 6 shows the structure and the configuration of a CVD

system of the third operation gestalt. The main components of a CVD system are a reaction chamber 1, the material gas feed zone 31, and the cleaning gas supply section 33. In a reaction chamber 1, desired Ti oxide, Zr oxide, Hf oxide, or the metal oxide film of such bipolar membrane is formed to a wafer 5.

[0062] Supply of material gas is the same as that of the first operation gestalt. That is, in the material gas feed zone 31, after the amount of requests evaporates the liquid raw material 14 extruded by the pressure of helium gas 17 with a carburetor 16, it is introduced in a reaction chamber 1. Piping 41 is heated to desired temperature (about 100-200 degrees C) so that material gas may not liquefy. In addition, the amount of requests can also supply O₂ gas 18 in a reaction chamber 1 with a massflow controller 19.

[0063] In the cleaning gas supply section 33 in this operation gestalt, a massflow controller 25 adjusts ClF gas 35 in the amount of requests, and it introduces in a reaction chamber 1 through a charging line.

[0064] (One) membrane formation activity (two or more sheet wafer processing), (2) cleaning activities, and (3) Puri membrane formation activity are successively repeated like [the CVD system of this third operation gestalt] the above-mentioned first and second operation gestalten.

[0065] About the procedure of the membrane formation activity of the above (1), since it is the same as that of the above-mentioned first operation gestalt, explanation is omitted. One by one, if this membrane formation processing activity is repeated, a metallic oxide will accumulate on the internal surface of a reaction chamber 1 as well as wafer 5 front face. This deposit becomes easy to separate in the stress which thermal stress and the film itself have from a wall surface, so that alimentation increases. The deposit which separated adheres to a wafer front face in gravity, electrostatic force, and a fluid force, and causes an open circuit and short circuit of wiring. Therefore, before becoming such a situation, cleaning for removing a deposit and defecating the inside of a reaction chamber 1 is carried out.

[0066] The procedure of cleaning of the above (2) is explained. Since installation of the covering wafer 40, setting out of the request temperature (about 200-700 degrees C) of a susceptor 3 and the request temperature (- 300 degrees C) of reaction chamber 1 wall surface and the shower head 6, etc. are the same as that of the above-mentioned first and second operation gestalten, explanation is omitted.

[0067] With this operation gestalt, under such temperature setting out, if the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa) with a vacuum pump 12 while introducing ClF gas 35 in the amount reaction chamber 1 of requests from the cleaning gas supply section 33, when ClF gas 35 is activated with heat energy, etching clearance of the deposit will be carried out and the inside of a reaction chamber 1 will be cleaned.

[0068] Since Cl remains on reaction chamber 1 wall surface after cleaning and ***** possibility is in the next membrane formation about an adverse effect, Like the operation gestalt of the above second, while introducing the hydrogen gas 21 of the cleaning gas supply section into a reaction chamber 1 after exhausting the cleaning gas in a reaction chamber 1 If the inside of a reaction chamber 1 is made into a desired pressure (several 10000Pa), Residual Cl will react with H and will be exhausted outside a reaction chamber as HCl gas.

[0069] Then, like the above-mentioned first and second operation gestalten, a susceptor 3 is moved, the covering wafer 40 is taken out from the conveyance opening 10, and a gate valve 11 is closed. Now, cleaning is completed.

[0070] Thus, since Ti oxide deposited on the internal surface 2 of a reaction chamber 1, Zr oxide, Hf oxide, or the deposition film of such bipolar membrane is efficiently removable according to this operation gestalt, an equipment stop time can be shortened and it is effective in an equipment operating ratio being referred to as being able to improve.

[0071] Next, although the procedure of the Puri membrane formation activity of the above (3) is the same as that of the membrane formation activity of the above (1) almost, membrane formation conditions, such as membrane formation time amount, temperature, and a pressure, differ. When the object of this activity makes containment and a front face smooth for the residual gas of the reaction chamber internal surface 2 after cleaning, it is as above-mentioned that it is for securing the stability of future membrane formation.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the relation between the temperature of Zr compound, and vapor pressure.

[Drawing 2] It is drawing showing the relation between the temperature of Hf compound, and vapor pressure.

[Drawing 3] It is drawing showing the relation between the temperature of Ti compound, and vapor pressure.

[Drawing 4] It is the sectional view showing the body of the semiconductor fabrication machines and equipment which are the 1st operation gestalten of this invention.

[Drawing 5] It is the sectional view showing the body of the semiconductor fabrication machines and equipment which are the 2nd operation gestalten of this invention.

[Drawing 6] It is the sectional view showing the body of the semiconductor fabrication machines and equipment which are the 2nd operation gestalten of this invention.

[Description of Notations]

- 1 Reaction Chamber
- 2 Internal Surface
- 3 Susceptor
- 5 Si Wafer
- 6 Shower Head
- 10 Conveyance Opening
- 12 Vacuum Pump
- 14 Liquid Raw Material
- 15 Liquid Massflow Controller
- 16 Carburetor
- 17 Helium Gas
- 18 O2 Gas
- 19, 23, 25 Massflow controller
- 20 Cl2 Gas
- 21 H2 Gas
- 22 Ar Gas
- 24 Source of Remote Plasma
- 26 Cleaning Gas Supply Piping
- 27 RF Matching Box
- 28 RF Power Source
- 29 Electric Insulating Plate
- 31 Material Gas Feed Zone
- 32 33 Cleaning gas supply section
- 34 RF Plasma Section

35 ClF3 Gas
40 Covering Wafer
41 Piping

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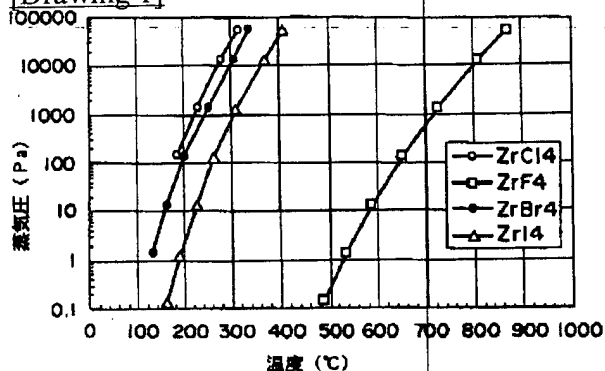
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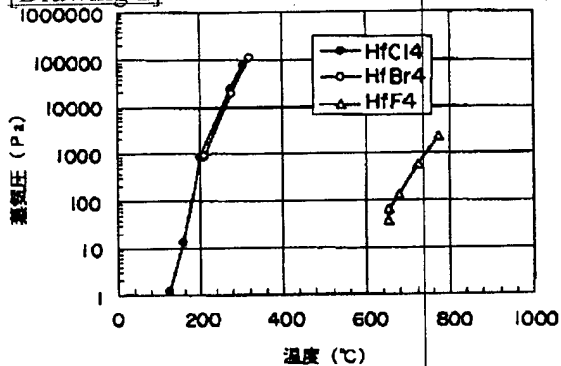
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DRAWINGS

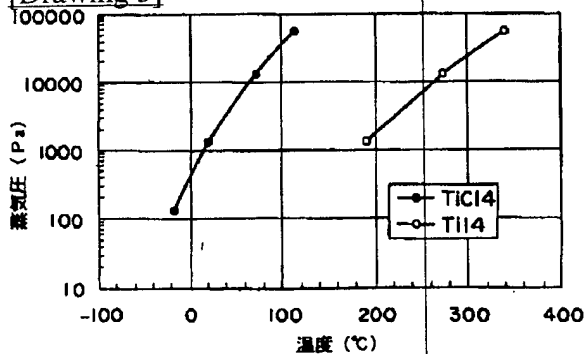
[Drawing 1]



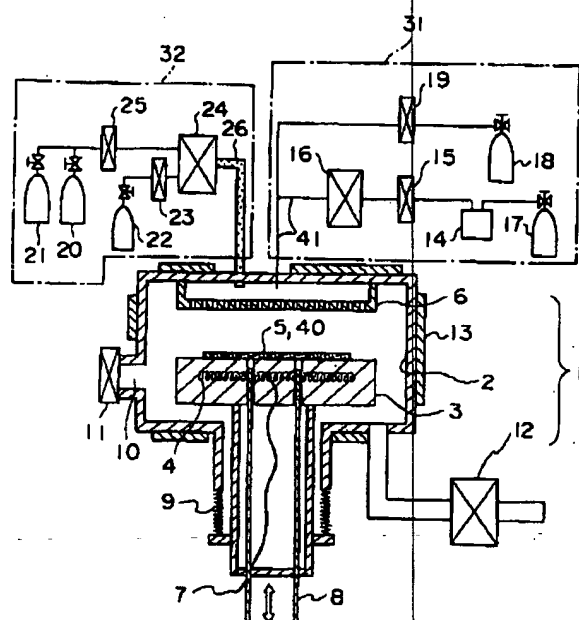
[Drawing 2]



[Drawing 3]

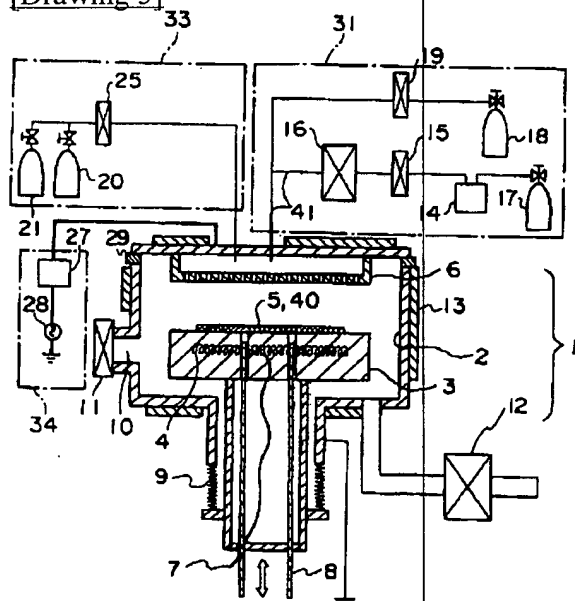


[Drawing 4]

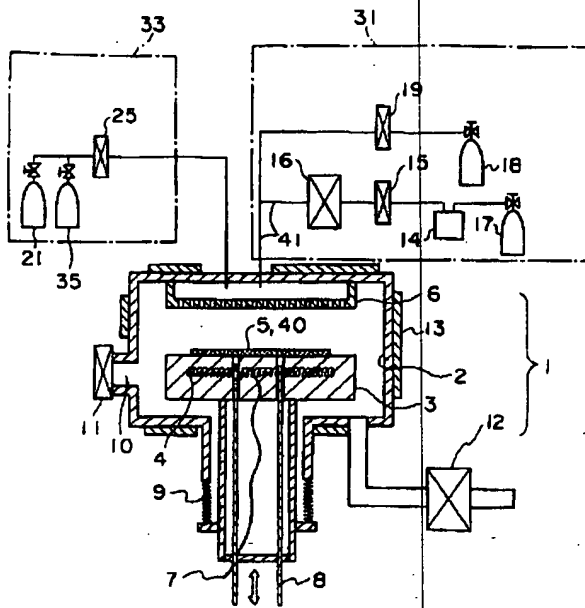


- 1: 反応室 2: 内壁面 3: サセプタ 5: Siウエハ 12: 真空ポンプ
 14: 液体原料 15: 液体マスフローコントローラ 16: 気化器
 17: Heガス 18: O₂ガス 19, 23, 25: マスフローコントローラ
 20: Cl₂ガス 21: H₂ガス 22: Arガス 24: リモートプラズマ源
 26: クリーニングガス供給配管 31: 原料ガス供給部
 32: クリーニングガス供給部 40: カバーウエハ 41: 配管

[Drawing 5]



[Drawing 6]



[Translation done.]

EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

PUBLICATION NUMBER : 2003203907
PUBLICATION DATE : 18-07-03

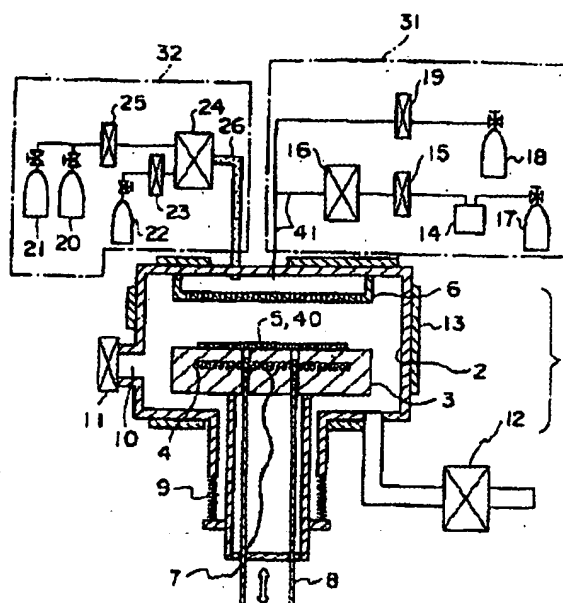
APPLICATION DATE : 07-01-02
APPLICATION NUMBER : 2002000217

APPLICANT : HITACHI KOKUSAI ELECTRIC INC;

INVENTOR : ASAI MASAYUKI

INT.CL. : H01L 21/31 C23C 16/44

TITLE : CVD SYSTEM AND CLEANING METHOD THEREFOR



- 1 : 反応室 2 : 内壁面 3 : サセプタ 5 : S i ウエハ 12 : 真空ポンプ
14 : 液体原料 15 : 液体マスフローコントローラ 16 : 気化器
17 : H₂ガス 18 : O₂ガス 19, 23, 25 : マスフローコントローラ
20 : Cl₂ガス 21 : H₂ガス 22 : Arガス 24 : リモートプラズマ源
26 : クリーニングガス供給配管 31 : 原料ガス供給部
32 : クリーニングガス供給部 40 : カバーウエハ 41 : 配管

ABSTRACT : PROBLEM TO BE SOLVED: To provide a CVD systems for efficiently removing Ti oxide, Zr oxide, Hf oxide, which are deposited on the inner wall face of a reaction chamber or the composite film of them, and to provide a cleaning method.

SOLUTION: In a cleaning gas supply part 32, chlorine gas containing chlorine, such as Cl₂, BCl₃, HCl, ClF₃ and ClF, is activated and is introduced into the reaction chamber 1. A deposited film is gasified and is removed. Since foreign matters attached to a wafer can be reduced by efficiently removing the deposited film on the inner wall face 2 of the reaction chamber 1, device stop time can be shortened and device operation rate is improved.

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DERWENT- 2003-622143
ACC-NO:

DERWENT- 200652
WEEK:

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TITLE: Chemical vapor deposition apparatus cleaning for semiconductor device manufacture, involves activating chlorine gas introduced into reaction chamber, so as to remove composite metal oxide film deposited in silicon wafer

PRIORITY-DATA: 2002JP-0000217 (January 7, 2002)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 3806868 B2	August 9, 2006	N/A	012	H01L 021/02
JP <u>2003203907</u> A	July 18, 2003	N/A	009	H01L 021/31

INT-CL (IPC): C23C016/44, H01L021/02 , H01L021/31

ABSTRACTED-PUB-NO: JP2003203907A

BASIC-ABSTRACT:

NOVELTY - A composite metal oxide film selected from a group comprising titanium, zirconium and hafnium oxides, is deposited on the surface of a silicon wafer (5) provided inside a reaction chamber. Chlorine gas (20) is introduced into the chamber and activated using plasma or heat energy, to remove the metal oxide film from the wafer.

DETAILED DESCRIPTION - An **INDEPENDENT CLAIM** is also included for a chemical vapor deposition apparatus.

USE - Used for cleaning a chemical vapor deposition (CVD) apparatus used for semiconductor device manufacture.

ADVANTAGE - Since chlorine gas is used for removing a composite metal oxide film from the silicon wafer, damage at the time of cleaning the reaction chamber is suppressed, reducing the cost and cleaning time effectively, improving the operating rate of the CVD apparatus.

DESCRIPTION OF DRAWING(S) - The figure shows a sectional view of the semiconductor manufacture apparatus. (Drawing includes non-English language text).

Reaction chamber 1

Inner wall of chamber 2

Silicon wafer 5

Vacuum pump 12

Chlorine gas supply unit 32

PAT-NO: JP02003203907A
DOCUMENT-IDENTIFIER: JP 2003203907 A
TITLE: CVD SYSTEM AND CLEANING METHOD THEREFOR
PUBN-DATE: July 18, 2003

INVENTOR-INFORMATION:

NAME	COUNTRY
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WATANABE, TOMOJI	N/A
KAGATSUME, AKIKO	N/A
NOUCHI, HIDEHIRO	N/A
ITAYA, HIDEJI	N/A
FUJIMOTO, TAKAYUKI	N/A
ASAI, MASAYUKI	N/A

ASSIGNEE-INFORMATION:

NAME	COUNTRY
HITACHI LTD	N/A
HITACHI KOKUSAI ELECTRIC INC	N/A

APPL-NO: JP2002000217
APPL-DATE: January 7, 2002

INT-CL (IPC): H01 L 021/31 , C23 C 016/44

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a CVD systems for efficiently removing Ti oxide, Zr oxide, Hf oxide, which are deposited on the inner wall face of a reaction chamber or the composite film of them, and to provide a cleaning method.

SOLUTION: In a cleaning gas supply part 32, chlorine gas containing chlorine, such as Cl

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STN Columbus

integrated circuit, which includes performing a capacitor stack etch to define the FeRAM capacitor. The method comprises etching a PZT ferroelec. layer with a high temp. **BC13** etch which provides substantial selectivity with respect to the hard mask. Alternatively, the PZT ferroelec. layer is etched using a low temp. **fluorine** component etch chem. such as CHF3 to provide a non-vertical PZT sidewall profile. Such a profile prevents conductive material assocd. with a subsequent bottom electrode layer etch from depositing on the PZT sidewall, thereby preventing leakage or a "shorting out" of the resulting FeRAM capacitor.

L17 ANSWER 14 OF 26 CAPLUS COPYRIGHT 2007 ACS on STN

Full Text

AN 2003:550695 CAPLUS

DN 139:109995

TI CVD apparatus and **cleaning** process thereof

IN Hoshino, Masakazu; Watanabe, Satoshi; Kagatsume, Akiko; Nouchi, Hidehiro; Itaya, Shuji; Fujimoto, Takayuki; Asai, Masayuki

PA Hitachi Ltd., Japan; Hitachi Kokusai Electric Inc.

SO Jpn. Kokai Tokkyo Koho, 9 pp.

CODEN: JKXXAF

DT Patent

LA Japanese

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2003203907	A	20030718	JP 2002-217	20020107
	JP 3806868	B2	20060809		
PRAI	JP 2002-217		20020107		

AB The title **cleaning** process involves (1) introducing Cl-contg. **cleaning** gas into the contaminant-deposited app., (2) activating the **cleaning** gas in the app., and (3) gasifying the deposits by reacting with the activated **cleaning** gas and removing the gasified deposits. The deposits on the app. wall may include Ti oxides, Zr oxides, Hf oxides, or their mixts. The Cl-contg. **cleaning** gas may include Cl2, **BC13**, HCl, **ClF3**, and/or ClF.

L17 ANSWER 15 OF 26 CAPLUS COPYRIGHT 2007 ACS on STN

Full Text

AN 2003:434954 CAPLUS

DN 138:394347

TI Method and system for providing high flux of point of use activated reactive species for semiconductor processing

IN Sandhu, Gurtej S.; Doan, Trung T.

PA Micron Technology, Inc., USA

SO U.S. Pat. Appl. Publ., 11 pp.

CODEN: USXXCO

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2003102008	A1	20030605	US 2001-998073	20011130
	US 7001481	B2	20060221		
	US 2004020511	A1	20040205	US 2003-392940	20030320
	US 6793736	B2	20040921		
PRAI	US 2001-998073	A3	20011130		

AB The invention relates to a method and system for providing high flux of point of use activated reactive species for semiconductor processing. A workpiece is exposed to a gaseous atm. contg. a transmission gas that is nonattenuating to preselected wavelengths of electromagnetic radiation. A

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号
特開2003-203907
(P2003-203907A)

(43)公開日 平成15年 7月18日 (2003. 7. 18)

(51)Int.Cl.⁷

識別記号

F I

テマコード* (参考)

H 0 1 L 21/31

H 0 1 L 21/31

C 4 K 0 3 0

C 2 3 C 16/44

C 2 3 C 16/44

J 5 F 0 4 5

審査請求 未請求 請求項の数 9 O L (全 9 頁)

(21)出願番号 特願2002-217(P2002-217)

(22)出願日 平成14年 1月 7日 (2002. 1. 7)

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東京都中野区東中野三丁目14番20号

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弁理士 吉岡 宏嗣

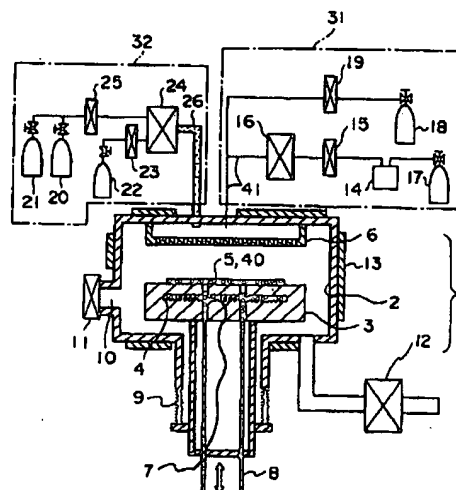
最終頁に続く

(54)【発明の名称】 CVD装置およびそのクリーニング方法

(57)【要約】

【課題】 反応室内壁面に堆積するTi酸化物、Zr酸化物、Hf酸化物、または、これらの複合膜を効率的に除去できるCVD装置およびそのクリーニング方法を提供する。

【解決手段】 クリーニングガス供給部32で、 Cl_2 、 BCl_3 、 HCl 、 ClF_3 、 ClF 等の塩素を含む塩素系ガスを活性化して反応室1内に導入して化学反応で堆積膜をガス化させて除去する。これにより、反応室1の内壁面2の堆積膜を効率的に除去することで、ウエハ付着異物が低減できるため、装置停止時間が短縮でき装置稼働率が向上する。



1:反応室 2:内壁面 3:サセプタ 5:Siウエハ 12:真空ポンプ
14:固体原料 15:液体マスフローコントローラ 16:酸化炉
17:H₂ガス 18:O₂ガス 19,23,25:マスフローコントローラ
20:Cl₂ガス 21:H₂ガス 22:Arガス 24:リモートプラズマ源
26:クリーニングガス供給ポート 31:原料ガス供給部
32:クリーニングガス供給部 40:カバーウエハ 41:磁石

【特許請求の範囲】

【請求項1】 反応室内のウエハ基板に、Ti（チタン）酸化物、Zr（ジルコニウム）酸化物、もしくはHf（ハフニウム）酸化物からなる金属酸化膜、または、これらの酸化物の2種以上を含む複合金属酸化膜を形成するCVD装置のクリーニング方法において、前記反応室の内部に堆積した前記金属酸化膜または前記複合金属酸化膜に、フッ素を含まない塩素原子を含む塩素系ガスを接触させることにより、該金属酸化膜または該複合金属酸化膜をエッチングして反応室内を清浄にすることを特徴とするCVD装置のクリーニング方法。

【請求項2】 請求項1に記載のCVD装置のクリーニング方法において、前記反応室の外で、前記塩素系ガスをプラズマもしくは熱エネルギーを用いて活性化することを特徴とするCVD装置のクリーニング方法。

【請求項3】 請求項1に記載のCVD装置のクリーニング方法において、前記反応室内で、前記塩素系ガスをプラズマもしくは熱エネルギーを用いて活性化することを特徴とするCVD装置のクリーニング方法。

【請求項4】 請求項1～3のうちいずれか1項に記載のCVD装置のクリーニング方法において、前記塩素系ガスは、 Cl_2 、 BCl_3 、 HCl のうちの、少なくとも一種のガスを選択して用いることを特徴とするCVD装置のクリーニング方法。

【請求項5】 反応室内のSiウエハ基板に、Ti（チタン）酸化物、Zr（ジルコニウム）酸化物、もしくはHf（ハフニウム）酸化物からなる金属酸化膜、または、これらの酸化物の2種以上を含む複合金属酸化膜を形成するCVD装置のクリーニング方法において、第1ステップとして、前記反応室内に堆積した前記金属酸化膜または前記複合金属酸化膜に、塩素原子を含む塩素系ガスを接触させることにより、該金属酸化膜または該複合金属酸化膜をエッチングし、第2ステップとして、塩素と反応し易いガスを反応室内に導入することを特徴とするCVD装置のクリーニング方法。

【請求項6】 請求項5に記載のCVD装置のクリーニング方法において、前記第2ステップで用いる塩素と反応し易いガスは、水素ガスまたは水蒸気のいずれか一方もしくは双方を用いることを特徴とするCVD装置のクリーニング方法。

【請求項7】 請求項1～6のうちいずれか1項に記載のクリーニング方法によって、反応室内がクリーニングされるCVD装置。

【請求項8】 反応室内のウエハ基板に、Ti（チタン）酸化物、Zr（ジルコニウム）酸化物、もしくはHf（ハフニウム）酸化物からなる金属酸化膜、または、これらの酸化物の2種以上を含む複合金属酸化膜を形成するCVD装置において、前記反応室の内部に堆積した前記金属酸化膜または前記複合金属酸化膜に接触させる塩素系ガスを、前記反応室の外でプラズマもしくは熱エ

ネルギーを用いて活性化する活性化手段を有することを特徴とするCVD装置。

【請求項9】 反応室内のウエハ基板に、Ti（チタン）酸化物、Zr（ジルコニウム）酸化物、もしくはHf（ハフニウム）酸化物からなる金属酸化膜、または、これらの酸化物の2種以上を含む複合金属酸化膜を形成するCVD装置において、前記反応室の内部に堆積した前記金属酸化膜または前記複合金属酸化膜に接触させる塩素系ガスを、前記反応室内でプラズマもしくは熱エネルギーを用いて活性化する活性化手段を有することを特徴とするCVD装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はCVD装置およびそのクリーニング方法に係り、特に、Siウエハ等の基板に、Ti酸化物、Zr酸化物、Hf酸化物、または、これらの複合酸化膜から選択した金属酸化物を形成するCVD（Chemical Vapor Deposition）装置の清浄化技術に関する。

【0002】

【従来の技術】半導体装置の消費電力を減らすために、 SiO_2 ゲート絶縁膜の薄膜化が進められている。 SiO_2 ゲート絶縁膜が薄膜化すると次のような問題が生じる。つまり、ゲート電極とチャネル層との間の直接トンネル効果による漏れ電流が増加し、さらには、ゲート絶縁膜の絶縁破壊の信頼性が低下する。

【0003】この問題を解決するために、 SiO_2 に代わる材料として、物理的に厚い膜を用いても、 SiO_2 と同じ静電容量が得られる高誘電率材料の適用検討が進んでいる。これにより、漏れ電流や絶縁破壊を抑えることができる。この高誘電率ゲート絶縁膜材料としては、具体的には、Ti酸化物、Zr酸化物、Hf酸化物、または、これらの複合物等の熱力学的に安定な酸化物の採用が検討されている。

【0004】これらの金属酸化物をウエハなどの基板に成膜するCVD装置では、反応室の内壁面などにもウエハ表面と同様に金属酸化物が堆積する。この堆積物は堆積量が増加するほど、熱応力や膜自身が持つ応力で壁面から剥がれ易くなる。剥がれた堆積物は、重力、静電気力、流体力などによりウエハ表面に付着して、配線の断線や短絡を引き起こす。そのため、このような問題が起こる前に、堆積物を定期的に除去（クリーニング）する必要がある。

【0005】このクリーニング方法として、最近では、特開平10-199874号公報に示すように、反応室とは別の場所に設けたプラズマ源を用いてラジカルを生成し、このラジカルを反応室内に導入することで、壁面堆積膜をエッチングしてクリーニングする、いわゆるリモートプラズマクリーニングが多用されている。この方法の特徴は、活性化したガスの化学反応だけで堆積物をガ

ス化してクリーニングするため、クリーニング時の壁面に対するイオンスパッタ等によるダメージが無いことである。

【0006】また、特開平10-335318号公報には、アルカリ土類金属を構成元素中に含む薄膜を対象として、ハロゲンあるいはハロゲン化合物を含むガスでクリーニングする方法が記載されている。

【0007】

【発明が解決しようとする課題】しかしながら、上記特開平10-199874号公報に記載のリモートプラズマクリーニングでは、従来からクリーニングガスとして多用されている NF_3 ガスを用いて、Zr酸化物、Hf酸化物、または、この複合膜をクリーニングしようとすると、反応生成物として、 ZrF_4 、 HfF_4 などが生成される。

【0008】これらの反応生成物の蒸気圧は非常に低く、例えば、 ZrF_4 の場合、蒸気圧は500℃で約0.1Pa、200℃ではほぼゼロである。CVD装置のクリーニング時の壁面温度が200℃以下であることを考えると、反応生成物が気化しないため、堆積物をクリーニングできないことになる。この問題を回避するためには、クリーニング時に化学反応により生成される反応生成物の蒸気圧が高いクリーニングガスを選択することが必要となる。

【0009】また、上記特開平10-335318号公報に記載の例は、クリーニング対象物がアルカリ土類金属であって本発明とは全く異なるが、Ti、Zr、もしくはHfなどの金属酸化膜、または、これらの複合金属酸化膜について、低温でクリーニングを行なう場合、ハロゲン化合物、例えば NF_3 ガスを、Zr酸化物のクリーニングに用いた場合、反応生成物の ZrF_4 の蒸気圧が低いと、低温では反応生成物が気化されず、クリーニングできないという問題点を有している。

【0010】本発明の目的は、CVD装置の反応室内の壁面などに堆積するTi酸化物、Zr酸化物、Hf酸化物およびこれらの複合物膜の熱力学的に安定な高誘電率材料を、エッチングで除去して反応室内を清浄化するCVD装置およびそのクリーニング方法を提供することにある。

【0011】

【課題を解決するための手段】上記目的を達成するために、本発明のCVD装置のクリーニング方法は、反応室内のウエハ基板上に、Ti（チタン）酸化物、Zr（ジルコニウム）酸化物、もしくはHf（ハフニウム）酸化物からなる金属酸化膜、または、これらの酸化物の2種以上を含む複合金属酸化膜を形成するCVD装置のクリーニング方法において、前記反応室の内部に堆積した前記金属酸化膜または前記複合金属酸化膜に、フッ素を含まない塩素原子を含む塩素系ガスを接触させることにより、該金属酸化膜または該複合金属酸化膜をエッチング

して反応室内を清浄にすることを特徴とする。

【0012】本発明者らの知見によれば、Ti、Zr、およびHfのハロゲン化物の蒸気圧と温度との関係を調べた結果、 ZrF_4 、 HfF_4 （フッ化物）に比べて、 ZrCl_4 、 HfCl_4 （塩化物）の蒸気圧ははるかに高く、200℃で蒸気圧が100Pa程度であり、クリーニング時の反応生成物をガス化できることが分かる（図1、2参照）。さらに、 TiCl_4 （塩化物）の蒸気圧は100℃で10000Pa以上あり、クリーニングに十分な蒸気圧のあることが分かる（図3）。

【0013】また、塩素原子とTi酸化物、Zr酸化物、Hf酸化物およびこれらの複合膜の金属酸化物の反応で、塩化物を生成する反応は、何れも反応前後のギブス自由エネルギーの差が負の値となり、金属酸化物と塩素系クリーニングガスとの反応が進み易いことがわかる。

【0014】以上のことから、本発明によれば、CVD装置の反応室内に堆積するTi酸化物、Zr酸化物、Hf酸化物およびこれらの複合膜の金属酸化物に、 NF_3 等のフッ素系のガスではなく、塩素系のガスを接触させてエッチングしたときに生成する反応生成物を迅速にガス化できる。したがって、このガスを排気すれば反応室内を容易に清浄化できる。

【0015】また、本発明における上記塩素系ガスの活性化は、反応室の内外で可能であり、CVD装置として上記塩素系ガスの活性化手段を、反応室の外に設置することにより、例えば、リモートプラズマクリーニングが可能となり、反応室内のクリーニング時のダメージが抑制される。また、反応室内で活性化させれば、装置の簡略化と低コスト化が可能となる。

【0016】

【発明の実施の形態】まず、本発明のCVD装置のクリーニング方法について、その概略を説明する。本発明においてエッチング除去する対象生成物は、Ti酸化物、Zr酸化物、Hf酸化物およびこれらの複合物の金属酸化物である。

【0017】本発明のクリーニング方法は、上記金属のフッ化物の蒸気圧に比較して、塩化物の蒸気圧の方が高い点に着目し、CVD装置（成膜装置）の反応室内に堆積する上記クリーニング対象生成物に、塩素系ガスを作用させてエッチング除去するようにしたものである。

【0018】以下、本発明のクリーニング方法について詳述する。半導体製造装置などのCVD装置の反応室内壁面に堆積する、Ti酸化物、Zr酸化物、Hf酸化物およびこれらの複合物の金属酸化物を、エッチング除去して反応室内を清浄化するためのクリーニングガスには、① クリーニングによる反応生成物の蒸気圧が高いこと、② 金属酸化物とクリーニングガスが反応し易いこと、の二つの条件が必要である。

【0019】まず、上記①の反応生成物の蒸気圧を検討する。一般に、クリーニングでは、反応性の高い塩素や

フッ素等を含むハロゲンガスが用いられる。そこで、Ti、Zr、およびHfのハロゲン化物の蒸気圧と温度との関係を調べた。その結果を図1～図3に示す。

【0020】図1および図2から、 ZrF_4 、 HfF_4 （フッ化物）に比べて、 $ZrCl_4$ 、 $HfCl_4$ （塩化物）の蒸気圧ははるかに高く、200℃で蒸気圧が100Pa程度であり、クリーニング時の反応生成物をガス化できることが分かる。また、図3から、 $TiCl_4$ （塩化物）の蒸気圧は100℃で10000Pa以上あり、クリーニングに十分な蒸気圧のあることが分かる。

【0021】以上のことから、 NF_3 等のフッ素系のガスではなく、塩素系のガスを用いることにより、CVD装置の反応室内壁面に堆積するTi酸化物、Zr酸化物、Hf酸化物およびこれらの複合膜の金属酸化物をエッチングしたときの反応生成物をガス化して排気できることが分かる。

【0022】次に、上記②の上記金属酸化物とクリーニングガスとの反応の進み易さについて検討する。反応の進み易さは、各金属酸化物と塩素原子、および反応生成物のそれぞれについてギブスの自由エネルギーを計算し、反応後の系のギブス自由エネルギーから、反応前の系のギブス自由エネルギーを差し引いた値（ ΔG ）を指標にすることができる。この ΔG と反応平衡定数（K）は、Rを気体定数、Tを反応時の系の温度とすると、次式（1）の関係にある。

$$K \propto \exp(-\Delta G/RT) \quad \dots\dots (1)$$

【0024】この式から、 ΔG が0あるいは+の値であれば反応はほとんど進まず、逆に ΔG が-で、その値が大きいほど反応が進む傾向にあると言える。塩素原子とTi酸化物、Zr酸化物、Hf酸化物およびこれらの複合膜の金属酸化物の反応で、塩化物を生成する反応は、何れも ΔG が負の値となり、反応が進む。

【0025】以上のことから、CVD装置の反応室内壁面や配管などに堆積するTi酸化物、Zr酸化物、Hf酸化物およびこれらの複合膜の金属酸化物に、塩素および塩素を含む塩素系ガスを接触させることにより、これらの膜をエッチング除去して、反応室内を清浄化することができる。なお、悪影響を避けるためにクリーニングガスにはフッ素を含まないほうが好ましい。

【0026】次に、本発明のCVD装置の実施形態を、図4～図6を用いて説明する。第一の実施形態（図4参照）は、本発明における塩素系ガスを反応室の外部で活性化して反応室内に導入するものである。また、第二の実施形態（図5参照）は、反応室内に導入した塩素系ガスを活性化させるもので、外部に電源を用意すればよい。また、第三の実施形態（図6参照）は、加熱した反応室に塩素系ガスを導入し、温度によって塩素系ガスを活性化させるものである。

【0027】（第一実施形態）図4は、第一実施形態のCVD装置の構造と構成を示したものである。CVD装置は、反応室1、原料ガス供給部31およびクリーニングガス供給部32で構成される。反応室1内で、ウエハ基板5（単に、ウエハ5ともいう）に所望のTi酸化物、Zr酸化物、Hf酸化物、または、これらの複合膜の金属酸化物を成膜する。

【0028】また、反応室1の内壁面2などのクリーニングガスと接触する部位は、クリーニングによるダメージを低減するために、クリーニングガスに対して耐性のある材料または表面処理、例えば、アルマイト処理、フッカニッケル不動態処理などが施されている。

【0029】原料ガス供給部31では、液体原料14を気化して反応室1に送り込む。Heガス17の圧力で押し出された液体原料14は、液体マスフローコントローラ15により、所望量が気化器16に送り込まれる。送り込まれた液体原料14は高温に保持された気化器16内で気化する。

【0030】この気化した液体原料14は配管41を通して反応室1内に導入される。配管41は、気化した液体原料14が再液化しないように所望の温度（100～200℃程度）に加熱してある。この他、 O_2 ガス18もマスフローコントローラ19で所望量が反応室1内に供給できる。

【0031】クリーニングガス供給部32では、クリーニングガスをプラズマにより活性化して反応室1内に送り込む。本発明では Cl_2 ガス20をArガス22とともに、マスフローコントローラ23、25で所望量をリモートプラズマ源24に導入する。

【0032】リモートプラズマ源24（RFプラズマ、 μ 波プラズマなど）に導入された Cl_2 ガス20は、プラズマエネルギーで活性化され、内面がアルマイト処理されたクリーニングガス供給配管26を通して反応室1内に導入される。同様に、 H_2 ガス21とArガス22も活性化して、反応室1内に導入できる。

【0033】このCVD装置では、（1）複数枚のウエハを処理する本来の成膜作業と、（2）本発明におけるクリーニング作業と、（3）本来の成膜作業を行なうための準備作業であるプリ成膜作業とが、順次繰り返される。

【0034】まず、上記（1）の成膜作業の手順について説明する。サセプタ3を下げて、その上面位置を搬送口10の水平面位置にする。そして、ゲートバルブ11を開けて、図示しない搬送アームで、ウエハ5を搬送口10からサセプタ3上に移動し、押上棒8を上方に移動させることで、ウエハ5を搬送アームから受け取り、搬送アームを反応室1外に移動するとともにゲートバルブ11を閉じる。次に押上棒8を下げるとともにサセプタ3を成膜位置まで上方に移動させる。

【0035】このとき、サセプタ3内に埋め込まれたヒ

ータ4に、給電線7から電力を供給して、ウエハ5を所望の温度(200~700℃程度)に上昇させる。同様に、反応室壁面2とシャワーヘッド6も温調ユニット13で所望の温度(〜300℃)に上昇させておく。

【0036】このような温度設定のもとで、原料ガス供給部31から液体原料14を気化した所望量の原料ガスと、マスフローコントローラ19で所望量のO₂ガス18を反応室1内に導入するとともに、真空ポンプ12で反応室1内を所望の圧力(数100〜数10000Pa)にして、ウエハ5に必要時間(数分)成膜する。

【0037】所望膜厚を成膜した後、成膜ガス供給部31からのガス供給を停止して、反応室1内の成膜ガスを排気した後、サセプタ3を下げ、その上面位置を搬送口10の水平面位置にする。そして、押上棒8でウエハ5を上方に持ち上げ、ゲートバルブ11を開けて、図示しない搬送アームを搬送口10からサセプタ3上に移動し、押上棒8を下方に移動させることで、ウエハ5を搬送アームに載せる。そして、搬送アームを反応室1外に移動し、ゲートバルブ11を閉じる。

【0038】複数回、このウエハ成膜処理作業を繰り返すと、反応室1の内壁面2にもウエハ5表面と同様に金属酸化物が堆積する。この堆積物は堆積量が増加するほど、熱応力や膜自身が持つ応力で壁面から剥がれ易くなる。剥がれた堆積物は、重力、静電気力、流体力等でウエハ5表面に付着して、配線の断線や短絡を引き起こす。そのため、このような事態になる前に、堆積物を除去して反応室1内を清浄化するために次のクリーニング作業を実施する。

【0039】上記(2)の本発明のクリーニング作業の手順について説明する。サセプタ3を下げ、その上面位置を搬送口10の水平面位置にする。そして、ゲートバルブ11を開けて、図示しない搬送アームでアルミナ製等のカバーウエハ40を搬送口10からサセプタ3上に移動し、上方に移動させた押上棒8で、カバーウエハ40を搬送アームから受け取り、搬送アームを反応室1外に移動させてゲートバルブ11を閉じる。次に押上棒8を下げるとともにサセプタ3を成膜位置まで上方に移動させる。

【0040】このとき、サセプタ3内に埋め込まれたヒータ4に給電線7から電力を供給することにより、サセプタ3を所望の温度(200~700℃程度)にする。同様に、反応室壁面2とシャワーヘッド6も温調ユニット13で所望の温度(〜300℃)にする。

【0041】このような温度設定のもとで、クリーニングガス供給部32から活性化したClを所望量反応室1内に導入するとともに、真空ポンプ12で反応室1内を所望の圧力(数10000Pa)にして必要時間(数分)クリーニングする。クリーニング後の反応室壁面2には、Clが残留し、次の成膜に悪影響をおよぼす可能性がある。

【0042】そのため、クリーニング終了後、ガスの供給を停止して、反応室1内のクリーニングガスを排気した後、クリーニングガス供給部32のH₂(水素)ガス21を、マスフローコントローラ25で所望量をリモートプラズマ源24に導入し、プラズマエネルギーでH₂ガス21を活性化して反応室1に導入するとともに、真空ポンプ12で反応室1内を所望の圧力(数10000Pa)にして必要時間(数分)クリーニングする。これで反応室1壁面に残留するClがHと反応し、HClガスとして反応室1外に排気される。

【0043】その後、サセプタ3を下げ、その上面位置を搬送口10の水平面位置にして、押上棒8でカバーウエハ40を上方に持ち上げ、次に、ゲートバルブ11を開けて、図示しない搬送アームを搬送口10からサセプタ3上に移動し、押上棒8を下方に移動させることで、カバーウエハ40を搬送アームに載せる。そして、搬送アームを反応室1外に移動するとともにゲートバルブ11を閉じる。これで、クリーニング作業が終了する。

【0044】このように、本実施形態によれば、反応室1の内壁面2に堆積したTi酸化物、Zr酸化物、Hf酸化物、または、これらの複合膜の堆積膜を所望の温度で効率的に除去できるので、装置停止時間が短縮でき装置稼働率を向上できると言う効果がある。

【0045】なお、上記(3)のプリ成膜作業の手順は、成膜時間、温度、圧力等の成膜条件は異なるが、上記(1)の成膜作業とほぼ同様の作業手順なので、ここでは説明を省略する。この作業の目的は、クリーニング後の反応室内壁面2の残留ガスを封じ込め、表面を平滑にすることにより、以後の成膜の安定性を確保するためである。

【0046】(第二実施形態)図5は、第二実施形態のCVD装置の構造と構成を示したものである。CVD装置の主な構成要素は、反応室1、原料ガス供給部31、クリーニングガス供給部33、RFプラズマ部34である。

【0047】反応室1は、クリーニング時に反応室1内にRFプラズマが生成できるように、反応室上部を絶縁板29で電氣的に絶縁してある。この反応室上部に、RFプラズマ部34を構成するRF電源28とマッチングボックス27が接続されている。

【0048】原料ガス供給部31では、液体原料14を気化して反応室1に送り込む。Heガス17の圧力で押し出された液体原料14は、液体マスフローコントローラ15により、所望量が気化器16に送り込まれる。送り込まれた液体原料14は高温に保持された気化器16内で気化する。

【0049】この気化した液体原料14は配管41を通して反応室1内に導入される。配管41は、気化した液体原料14が液化しないように所望の温度(100~200℃程度)に加熱してある。この他、O₂ガス18も

マスフローコントローラ19で所望量反応室1内に供給できる。

【0050】クリーニングガス供給部33では、本発明におけるC1₂ガス20、およびH₂ガス21を、マスフローコントローラ25により所望量に調節して、供給配管を通して反応室1内に導入する。

【0051】この第二実施形態のCVD装置でも、第一実施形態と同様に、(1)成膜作業(複数枚ウエハ処理)、(2)クリーニング作業、(3)プリ成膜作業が順次繰り返される。

【0052】上記(1)の成膜作業の手順は、上記第一実施形態と同様である。順次、この成膜処理作業を繰り返すと、反応室1の内壁面にもウエハ5表面と同様に金属酸化物が堆積する。この堆積物は堆積量が増加するほど、熱応力や膜自身が持つ応力で壁面から剥がれ易くなる。

【0053】剥がれた堆積物は、重力、静電気力、流体力などによりウエハ表面に付着して、配線の断線や短絡を引き起こす。そのため、このような事態になる前に、堆積物を除去して反応室1内を清浄化するためのクリーニング作業を実施する。

【0054】上記(2)のクリーニング作業の手順について説明する。まず、サセプタ3を移動させ、カバーウエハ40を受け取り、成膜位置まで移動させる。このとき、サセプタ3内に埋め込まれたヒータ4でサセプタ3を所望の温度(200~700℃程度)にし、同様に、反応室1壁面とシャワーヘッド6も温調ユニット13で所望の温度(~300℃)にする。以上は、第一実施形態と同様なので詳細な説明は省略する。

【0055】このような温度設定のもとで、本実施形態では、塩素系クリーニングガスを反応室内で活性化させるために、クリーニングガス供給部33からC1₂ガス20の所望量を反応室1内に導入するとともに、真空ポンプ12で反応室1内を所望の圧力(数10000Pa)にする。

【0056】次いで、RF電源28からパワー(数100~数kW)を投入する。これにより、反応室1内にC1プラズマが生成され、活性化したC1が反応室1壁面の堆積物と反応することとスパッタ作用とにより、堆積物がエッチング除去されて反応室1内がクリーニングされる。クリーニング後の反応室1壁面には、C1が残留し、次の成膜に悪影響をおよぼす可能性がある。

【0057】そのため、クリーニング終了後、ガスの供給を停止して、反応室1内のクリーニングガスを排気した後、クリーニングガス供給部33のH₂ガス21をマスフローコントローラ25で所望量に調整して反応室1に導入するとともに、真空ポンプ12で反応室1内を所望の圧力(数10000Pa)にしてクリーニングする。これで、クリーニングにより反応室1壁面に残留するC1がHと反応し、HClガスとして反応室外に排気

される。

【0058】その後、第一実施形態と同様に、サセプタ3を移動させ、カバーウエハ40を搬送アームによって反応室1外に搬出し、ゲートバルブ11を閉じてクリーニング作業を終了する。

【0059】このように、本実施形態によれば、反応室1の内壁面2に堆積したTi酸化物、Zr酸化物、Hf酸化物、または、これらの複合膜の堆積膜を、所望の温度で効率的に除去できるので、装置停止時間が短縮でき装置稼働率を向上できるという効果がある。

【0060】上記(3)のプリ成膜作業の手順は、上記(1)の成膜作業とほぼ同様であるが、成膜時間、温度、圧力等の成膜条件は異なる。この作業の目的は、クリーニング後の反応室内壁面2の残留ガスを封じ込め、表面を平滑にすることにより、以後の成膜の安定性を確保するためである。

【0061】(第三実施形態)図6は、第三実施形態のCVD装置の構造と構成を示したものである。CVD装置の主な構成要素は、反応室1、原料ガス供給部31、クリーニングガス供給部33である。反応室1内で、ウエハ5に所望のTi酸化物、Zr酸化物、Hf酸化物、または、これらの複合膜の金属酸化物膜を成膜する。

【0062】原料ガスの供給は第一実施形態と同様である。すなわち、原料ガス供給部31では、Heガス17の圧力で押し出された液体原料14は、所望量が気化器16で気化した後、反応室1内に導入される。配管41は、原料ガスが液化しないように所望の温度(100~200℃程度)に加熱してある。その他、O₂ガス18もマスフローコントローラ19で所望量が反応室1内に供給できる。

【0063】本実施形態におけるクリーニングガス供給部33では、CIFガス35をマスフローコントローラ25で所望量に調整し、供給配管を通して反応室1内に導入する。

【0064】この第三の実施形態のCVD装置も、上記第一および第二の実施形態と同様に、(1)成膜作業(複数枚ウエハ処理)、(2)クリーニング作業、(3)プリ成膜作業が順次繰り返される。

【0065】上記(1)の成膜作業の手順については、上記第一実施形態と同様なので説明を省略する。順次、この成膜処理作業を繰り返すと、反応室1の内壁面にもウエハ5表面と同様に金属酸化物が堆積する。この堆積物は堆積量が増加するほど、熱応力や膜自身が持つ応力で壁面から剥がれ易くなる。剥がれた堆積物は、重力、静電気力、流体力でウエハ表面に付着して、配線の断線や短絡を引き起こす。そのため、このような事態になる前に、堆積物を除去して反応室1内を清浄化するためのクリーニング作業を実施する。

【0066】上記(2)のクリーニング作業の手順について説明する。カバーウエハ40の導入と、サセプタ3

の所望温度(200~700℃程度)、および、反応室1壁面とシャワーヘッド6の所望温度(〜300℃)の設定などは、上記第一および第二の実施形態と同様なので説明を省略する。

【0067】本実施形態では、このような温度設定のもとで、クリーニングガス供給部33からCIFガス35を所望量反応室1内に導入するとともに、真空ポンプ12で反応室1内を所望の圧力(数10000Pa)にすると、CIFガス35が熱エネルギーで活性化することにより、堆積物がエッチング除去されて反応室1内がクリーニングされる。

【0068】クリーニング後の反応室1壁面には、Clが残留し、次の成膜に悪影響をおよぼす可能性があるため、上記第二の実施形態と同様に、反応室1内のクリーニングガスを排気後、クリーニングガス供給部の水素ガス21を反応室1に導入するとともに、反応室1内を所望の圧力(数10000Pa)にすると、残留ClがHと反応し、HClガスとして反応室外に排気される。

【0069】その後、上記第一および第二の実施形態と同様に、サセプタ3を移動させ、カバーウエハ40を搬送口10から搬出してゲートバルブ11を閉じる。これで、クリーニング作業が終了する。

【0070】このように、本実施形態によれば、反応室1の内壁面2に堆積したTi酸化物、Zr酸化物、Hf酸化物、または、これらの複合膜の堆積膜を効率的に除去できるので、装置停止時間が短縮でき装置稼働率を向上できるという効果がある。

【0071】次に、上記(3)のプリ成膜作業の手順は上記(1)の成膜作業とほぼ同様であるが、成膜時間、温度、圧力等の成膜条件は異なる。この作業の目的は、クリーニング後の反応室内壁面2の残留ガスを封じ込め、表面を平滑にすることにより、以後の成膜の安定性を確保するためであることは、前述のとおりである。

【0072】

【発明の効果】以上述べたように、本発明によれば、CVD装置の反応室内の壁面などに堆積するTi酸化物、Zr酸化物、Hf酸化物およびこれらの複合物膜の熱力学的に安定な高誘電率材料を、エッチングにより効率的に除去できるので、装置停止時間が短縮でき装置稼働率を向上できるという効果がある。

【図面の簡単な説明】

【図1】Zr化合物の温度と蒸気圧との関係を示す図である。

【図2】Hf化合物の温度と蒸気圧との関係を示す図である。

【図3】Ti化合物の温度と蒸気圧との関係を示す図である。

【図4】本発明の第1実施形態である半導体製造装置の主要部を示す断面図である。

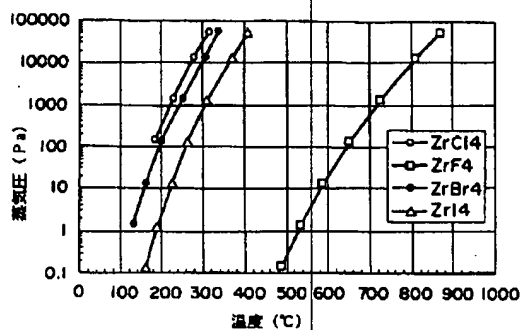
【図5】本発明の第2実施形態である半導体製造装置の主要部を示す断面図である。

【図6】本発明の第2実施形態である半導体製造装置の主要部を示す断面図である。

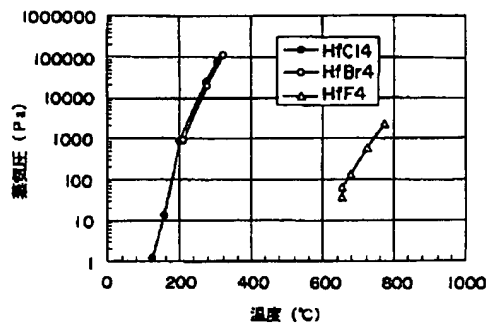
【符号の説明】

- 1 反応室
- 2 内壁面
- 3 サセプタ
- 5 Siウエハ
- 6 シャワーヘッド
- 10 搬送口
- 12 真空ポンプ
- 14 液体原料
- 15 液体マスフローコントローラ
- 16 気化器
- 17 Heガス
- 18 O₂ガス
- 19、23、25 マスフローコントローラ
- 20 Cl₂ガス
- 21 H₂ガス
- 22 Arガス
- 24 リモートプラズマ源
- 26 クリーニングガス供給配管
- 27 RFマッチングボックス
- 28 RF電源
- 29 絶縁板
- 31 原料ガス供給部
- 32、33 クリーニングガス供給部
- 34 RFプラズマ部
- 35 CIF₃ガス
- 40 カバーウエハ
- 41 配管

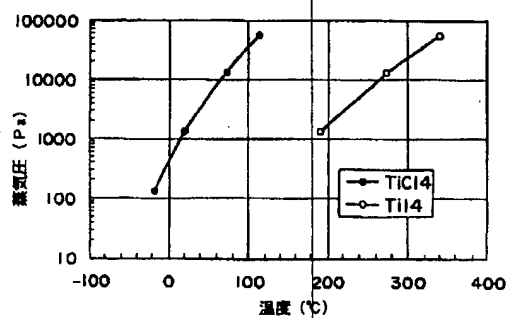
【図1】



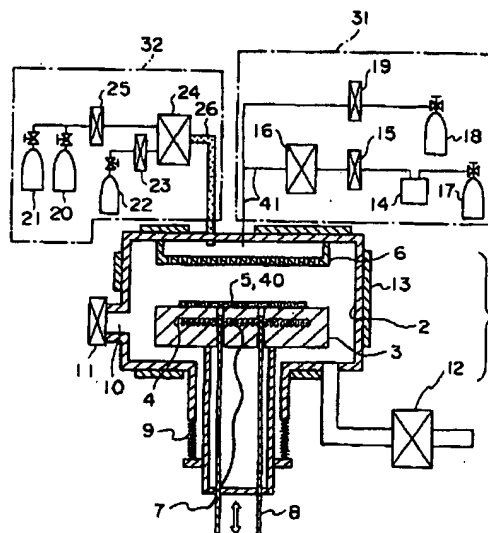
【図2】



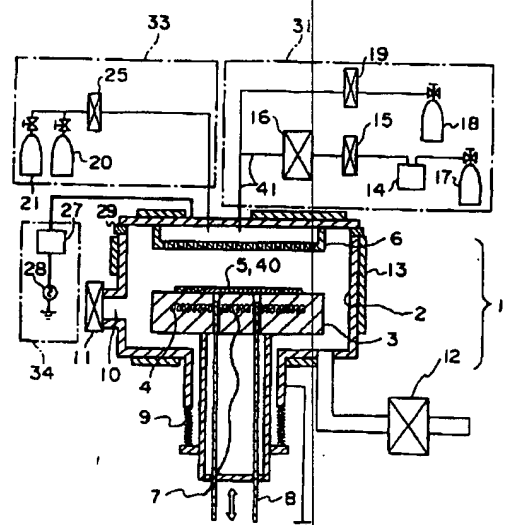
【図3】



【図4】

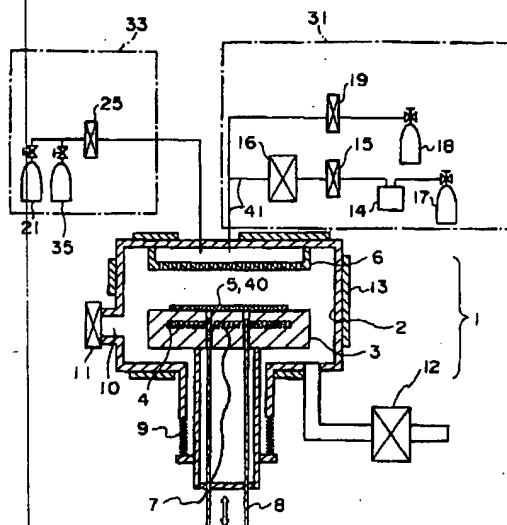


【図5】



- 1: 反応室 2: 内壁面 3: サセプタ 5: S i ウエハ 12: 真空ポンプ
 14: 液体原料 15: 液体マスフローコントローラ 16: 酸化剤
 17: Heガス 18: O₂ガス 19, 23, 25: マスフローコントローラ
 20: Cl₂ガス 21: H₂ガス 22: Arガス 24: リモートプラズマ源
 26: クリーニングガス供給配管 31: 原料ガス供給部
 32: クリーニングガス供給部 40: カバーウエハ 41: 配管

【図6】



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